A Study of some Co-ordination Chemistry of the Group IVA Elements

by

Douglas Gordon

A thesis submitted as part requirement for the degree of Doctor of Philosophy of the University of Warwick.

The work herein reported was carried out between October 1981 and September 1984, mostly in the Department of Chemistry and Molecular Sciences, though partly in the laboratories of Plastics and Petrochemicals Division, Imperial Chemical Industries PLC.

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ABSTRACT

Some co-ordination chemistry of the Group IVA chlorides was studied, with respect to the action of these elements as Ziegler-Natta catalysts.

Compounds of the type $MgCl_2 \cdot MCl_4 \cdot nL$ (L = EtOAc; n = 4, M = Ti, Zr, Hf, Sn; n = 2, M = Ti; n = 6, M = Th; and L = EtOFm, THF, n = 4, M = Ti) were prepared and studied using i.r. and n.m.r. spectroscopy. Observations indicate that several species co-exist in solutions of these compounds. The mixed compound $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12$ EtOAc was also prepared.

The mixed titanium chloro-carboxylates $TiCl_x(O_2CR)_{4-x}$ (x = 2, R = Me, CMe_3; x = 3, R = Me, CMe, Ph) were prepared and characterised. Hydrolysis reactions of these compounds in the solvents EtOAc and THF yielded compounds of the type $[TiCl_2(O_2CR) \cdot L]_2O$. An X-ray crystallographic study of the compounds $[TiCl_2(O_2CPh) \cdot L]_2O$ showed that two titanium atoms are bridged by two carboxylate groups and an oxygen atom.

Phosphine and amine complexes of the chlorides of titanium and zirconium were prepared and their reactions with reducing agents such as $LiBH_4$ and sodium amalgam were studied in an attempt to prepare stabilized low oxidation state compounds of these elements. Hence some complexes of $TiCl_4$, $TiCl_3$, $ZrCl_4$ and $(PhO)_2TiCl_2$ with the ligands PEt_3, PBu_3, DPPE, DMPE, DBPE and TMEDA were prepared and characterised using ^1H and ^{31}P n.m.r. spectroscopy. The reactions of these compounds were generally complex and difficult to resolve.

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ABBREVIATIONS

M	metal	L	ligand
R	alkyl	EtOAc	ethyl acetate
Me	methyl	EtOFm	ethyl formate
Et	ethyl	EtOBz	ethyl benzoate
Pr	propyl	DES	diethyl succinate
Bu	butyl	DEM	diethyl maleate
Ph	phenyl	DIBP	di-isobutyl phthalate
Cp	cyclopentadienyl	THF	tetrahydrofuran

DMPE	1,2 Bis-[dimethyl phosphino]ethane
DBPE	1,2 Bis-[dibutyl phosphino]ethane
DPPE	1,2 Bis-[diphenyl phosphino]ethane
TMEDA	1,2 Bis-[dimethyl amino]ethane
py	pyridine

spectra:

i.r.	infra-red	n.m.r.	nuclear magnetic resonance
s	strong	s	singlet
m	medium	d	doublet
w	weak	t	triplet
		m	multiplet
		b	broad

CHAPTER 1

1.0. INTRODUCTION

Interest in the chemistry of the Group IVA elements (titanium, zirconium and hafnium) has been sustained by industrial as well as academic chemists[1,2]. The interest of the former group arises largely because of the ability of these elements to promote, or catalyse, the reactions of organic molecules. Examples of these reactions include the reductive coupling of carbonyl compounds to diols or alkenes, and the many hydrozirconation reactions[3,4,5,6].

$$R_2C = O \xrightarrow{TiCl_3/LiAlH_4} R_2C = CR_2$$

$$Cp_2ZrHCl + R_2C = CR_2 + R^1X \rightarrow R_2HC - CXR_2$$

However, the most remarkable and widely used reaction that these elements, and titanium in particular, bring about is the polymerization of α-alkenes or dienes. These reactions are best carried out using a Ziegler-Natta type catalyst, which consists of a titanium halide in conjunction with an aluminium alkyl. In practice the halide used is normally titanium tetrachloride, and the alkyl is either diethyl aluminium chloride or aluminium triethyl. These reactions are discussed in more detail later (Chapter 2).

The high molecular weight products of these reactions are of considerable industrial interest, and consequently the investigation of the catalyst systems has generated a huge patent literature.

The work described in this thesis arises from the need to identify more clearly the nature of the species involved in a typical industrial Ziegler-Natta catalyst. The work has been carried out on a C.A.S.E. award with I.C.I. PLC (Plastics and Petrochemicals Division).

The main aim of this project has been to identify some of the titanium-containing molecular compounds which might be expected to be present in the catalyst prior to the addition of the aluminium alkyl. Although it would of course be highly desirable to be able to identify the active species containing both titanium and aluminium, the reactions which occur on the addition of the aluminium alkyl are both complex and numerous. Some advances have been made, as noted in Chapter 2, but in general the species present in the final catalytic mixture continue to defy attempts to characterise them. Of necessity therefore at this stage we are seeking to identify the titanium-containing precursors, as well as investigating some of their reactions. To this end about twenty-five new co-ordination compounds, mainly of titanium, have been characterised in the present work, and some of their properties, including precise structural details

using X-ray diffraction techniques, have been studied.

Since the predominant part of the work described herein involves the co-ordination chemistry of the Group IVA elements, often in non-aqueous solvents, the background chemistry of these compounds is discussed here, while more detailed information will be introduced in the appropriate chapters throughout the thesis. Since some of the studies in this thesis concern an investigation of the products arising from the hydrolysis of titanium chloride derivatives, it is relevant to include in this general introduction a brief discussion of the nature of titanium species which can occur under aqueous conditions.

Some co-ordination chemistry of tin tetrachloride has also been studied in the course of this work, because of the similarities between $SnCl_4$ and the Group IVA tetrachlorides, and $TiCl_4$ in particular. Therefore aspects of the co-ordination chemistry of $SnCl_4$ are also discussed in this chapter.

This introduction is therefore necessarily selective, and deals with those properties pertinent to the compounds studied in this thesis.

1.1 The Chemistry of Titanium

Titanium chemistry has been the subject of books by Clark[7], Cotton and Canterford[8], and Kepert[9]. The

organometallic chemistry of titanium has been the subject of books by Wailes, Coutts and Weigold[10] and Feld and Cowe[11]. In addition several sources continually update the area. Thus Annual Reports of the R.S.C. is an annual (but not comprehensive) review of all aspects of the chemistry of the Group IVA elements[12]. A comprehensive annual review of the co-ordination chemistry of titanium appears in Co-ordination Chemistry Reviews[13], and the organometallic compounds are surveyed annually in the Journal of Organometallic Chemistry, recent reviews being by Labinger[14].

In this introduction compounds in oxidation states (IV), (III) and (II) will be discussed under the four headings of oxidation states, aqueous chemistry, general properties of titanium halides and co-ordination chemistry of titanium chlorides.

Compounds with titanium in oxidation states (O) and (-1) are rare. These oxidation states are only found in the complexes of strong π-acid ligands, such as bipy, phosphines, butadiene and toluene. This type of compound will be discussed in Chapter 4.

1.2 Oxidation States (IV), (III) and (II) of Titanium

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$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$. In common with the other early transition elements titanium exhibits an oxidation state (IV), which involves the use in bonding of all the $4s^2 3d^2$ valence electrons. This is the most common oxidation state of titanium, and it is the one which is stable with respect to air. The combined effects of a high ionization potential (91.1 eV), and the highly polarising nature of a highly charged cation, mean that the Ti^{4+} ion does not exist, as such, and so the bonds in the compounds of Ti(IV) are essentially polar-covalent in character.

There is also an extensive chemistry of titanium(III), where the metal possesses a $3d^1$ electronic configuration. This is produced from titanium(IV) by the action of mild reducing agents,

$$Ti^{4+} + e \quad \rightleftarrows \quad Ti^{3+} \quad E^{o} = 0.1v$$

The equation above is a very crude representation of the species involved under many solution conditions, as solvolysis of the ions is virtually certain to take place in any polar co-ordinating solvent.

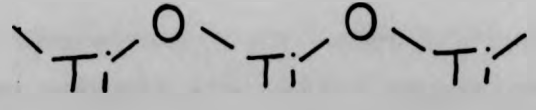
Few compounds of titanium(II) ($3d^2$) are known[7], and these are all strong reducing agents.

$$Ti^{2+}\ (aq) + e \rightarrow Ti^{3+}\ (aq) \quad E^{o} \sim 2.0\ V$$

1.3 Aqueous Chemistry of Titanium(IV)

The hydrated Ti^{4+} ion does not exist as such, as its high charge to size ratio makes it strongly polarising. Consequently Ti(IV) forms covalent compounds by the disruption of solvent molecules. The species present in aqueous solutions of Ti(IV) are dependent upon both pH and the counter ion, and are generally not well characterised.

Some species have been identified, for example, X-ray diffraction methods have established that the solid with the empirical formula $TiOSO_4.H_2O$ is polymeric, containing chains of alternating titanium and oxygen atoms which are interlinked by co-ordination of each titanium atom to three sulphate groups. One water molecule is also co-ordinated to each titanium which is thus six co-ordinate in an octahedral environment[15].



At high pH colloidal TiO_2 precipitates from aqueous solutions of Ti(IV).

Many compounds which were originally formulated as containing a Ti = O double bonded fragment in

in a "titanyl" cation, TiO^{2+}, have also been shown to be polymeric on the basis of evidence from infra-red spectra. Such species contain oxygen bridging two titanium centres. Examples of such polymeric species are the compounds $TiOX_2$ ($X=F^-$, Cl^-, Br^-, I^-, ClO_4^-, NO_3^-), and their adducts such as $TiOCl_2 \cdot 2py$ [16].

Polymeric structures were assigned to these compounds on the basis that the titanium-oxygen stretching frequencies in their infra-red spectra were below 700 cm^{-1}.

In compounds where the presence of a Ti=O moiety has been proven unambiguously, by X-ray diffraction methods, the titanium-oxygen stretching frequency has been assigned to a bond near 975 cm^{-1} in the infra-red spectrum. Examples of such complexes are $[R_4N]_2[TiOCl_4]$ (R = Me, Et) [17], which contain square pyramidal anions, in which the oxygen is at the apex of the pyramid, and the four chlorides are in the basal plane.

Some complexes such as TiO(phthalo-cyanine) [18] have been assigned a monomeric square pyramidal geometry, also on the basis of their infra-red spectra. Such derivatives have spectra which contain strong bands above 950 cm^{-1} which have been assigned to Ti = O stretching. The Ti = O unit has also been identified crystallographically in a porphyrin

complex[19]. There is square pyramidal co-ordination around the titanium atom in this complex. The titanium is 0.79Å above the centre of the plane of the four nitrogen donors, and the oxygen is the apex of the pyramid. The Ti = O distance of 1.62Å is short in comparison with other titanium-oxygen distances (~ 1.8Å).

Discrete molecular complexes, as opposed to the polymeric systems described above, containing oxygen atoms which bridge two titanium atoms are often formed in non-aqueous solvents, and will be discussed in detail in Chapter 3.

1.4 Aqueous Chemistry of Titanium(III)

In contrast to the chemistry of the Ti(IV) ion, the relatively larger and less polarizing Ti(III) shows distinct differences in its behaviour in aqueous solution (Ti^{4+}, 0.68; Ti^{3+}, 0.76Å). The purple hexaaquo ion, $[Ti(H_2O)_6]^{3+}$ has been identified in dilute acid solutions by visible spectroscopy. It has also been identified by crystallographic methods in the solid $CsTi(SO_4)_2.12H_2O$[20]. The cation $[Ti(H_2O)_4X_2]^+$ (X = Cl, Br) has been suggested to exist in the crystalline hexahydrates of $TiCl_3$ and $TiBr_3$, on the basis of evidence from infra-red, E.S.R., and visible spectra. Thus the electronic

spectrum of the hexaaquo ion consists of one strong band at 21,100 cm^{-1}, with a pronounced shoulder at 17,000 cm^{-1}, which can be explained in terms of the Jahn-Teller effect. However, the diffuse reflectance spectra of $[Ti(H_2O)_6X_3]$ (X = Cl, Br) shows that the absorption bands shift to lower frequencies, and comparison of these spectra with those of $[Ti(OH_2)_6]^{3+}$, and $[TiCl_6]^{3-}$ in $TiCl_3$, led to the conclusion that the species present were *trans*-$[Ti(OH_2)_4X_2]^+$ (X = Cl, Br)[21].

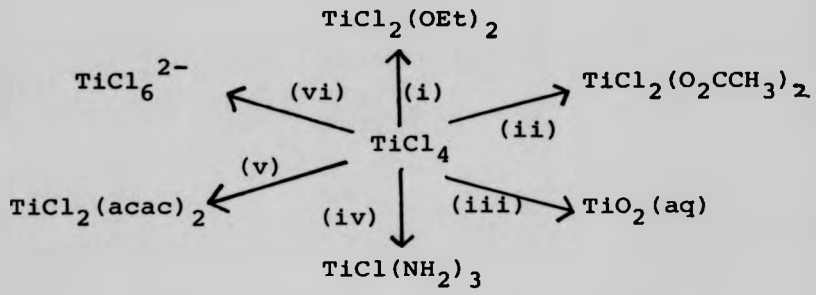
This conclusion is supported by evidence from the E.S.R. spectra of these solids[22].

1.5 General Properties of the Halides

By far the most widely studied compounds of titanium in non-aqueous solvents are the halides. This arises in part from their accessibility, and because they are sufficiently reactive to be convenient starting materials for the preparation of many other compounds, and particularly because they are strong Lewis acids, and form a large number of co-ordination compounds.

Although this work has concentrated on the chloride derivatives, the other halide derivatives are included in this discussion for comparative purposes. Some of their general reactions, exemplified by $TiCl_4$,

are shown below.



(i) EtOH (ii) CH_3CO_2H (iii) H_2O

(iv) NH_3 (v) Hacac (vi) conc. HCl

The tetrachloride is prepared by treating the dioxide with chlorine in the presence of a reducing agent, such as charcoal, at 1000°C.

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO$$

The other tetrahalides are most conveniently prepared from the tetrachloride. The tetrafluoride and tetrabromide can be prepared by carefully dropping $TiCl_4$ into the appropriate acid, HF or HBr. The tetraiodide is prepared similarly by passing HI gas through liquid $TiCl_4$

$$TiCl_4 + 4HX \rightarrow TiX_4 + 4HCl \quad (X=F, Br, I)$$

Titanium trichloride can be prepared by reduction of $TiCl_4$ with hydrogen gas.

$$2TiCl_4 + H_2 \xrightarrow{800^{\circ}C} 2TiCl_3 + 2HCl$$

All the tetrahalides can also be prepared by direct combination of the elements, and the trihalides can be prepared by reaction of the tetrahalides with titanium.

By using these methods the whole range of tri- and tetrahalides have been prepared (TiX_3, TiX_4; X = F, Cl, Br, I), and they have all been well characterised. Some of the properties of the tetrahalides are shown below:

TiX_4	colour	m.p.($^{\circ}C$)	b.p.($^{\circ}C$)	structure
F	white	-	284(sub)	F bridged polymer
Cl	colourless	-24.1	136	tetrahedral monomer
Br	orange	38.2	233	"
I	brown	155	377	"

1.6 Co-ordination Chemistry of the Titanium Tetrahalides

All the tetrahalides of titanium act as Lewis acids, but the relative strengths of their acceptor properties varies through the series. Hence enthalpies

of formation of the pyridine adducts, $TiX_4 2py$, in the gaseous state were calculated to be in the order

$$Cl > F > Br > I$$

on the basis of dissociation pressure measurements[28]. The anomalous position of the fluoride is discussed in section 1.6.1.

The tetrahalides can form both 1:1 and 1:2 complexes with unidentate ligands. The 1:1 adducts are most commonly octahedral halo-bridged dimers, though five co-ordinate trigonal bipyramidal species are known. The 1:2 adducts are commonly octahedral, and both *cis* and *trans* isomers are known.

With appropriate bidentate ligands (e.g. DIARS, $o\text{-}C_6H_4(AsMe_2)_2$) further co-ordination can occur to yield eight co-ordinate complexes with a dodecahedral geometry. Such co-ordination, although relatively rare for titanium, occurs more commonly with zirconium and hafnium, as might be expected from the relative covalent radii of the respective M(IV) atoms (Ti, 1.36; Zr, 1.45; Hf, 1.44Å), together with the promotion energies involved.

1.6.1 Titanium Tetrafluoride

Titanium tetrafluoride forms complexes less

readily than the other titanium tetrahalides. This is probably because TiF_4 is a strongly bonded fluoro-bridged polymer which is not easily disrupted by donors. The insolubility of 1:1 adducts of TiF_4 with ligands, such as amines, suggests that these complexes are also fluoro-bridged polymers[23].

Many 1:2 adducts of TiF_4 have been isolated, and ^{19}F n.m.r. spectroscopy has been useful in the elucidation of the structures of these compounds. Two well characterised series of adducts formed by TiF_4 are those involving derivatives of pyridine-1-oxide and ortho-substituted pyridine-1-oxides. With the former the 1:2 adducts were assigned a *cis* structure on the evidence that two distinct resonances were observed in their ^{19}F n.m.r. spectra[24]. However, when the latter ligands were used the 1:2 adducts contained some *trans* isomer, observed in solution as the minor product[25].

It was suggested that the *cis* isomers were favoured because this allowed the greatest d_π-p_π bonding from titanium to fluorine. The presence of d_π-p_π bonding in complexes of TiF_4 was suggested on the basis of a comparison of the ^{19}F n.m.r. spectra of the complexes *cis*-$TiF_4 \cdot 2C_2H_5OH$ and *cis*-$SnF_4 \cdot 2C_2H_5OH$ [24]. In the former case two well resolved resonances were observed, indicating a significant difference in the shielding of the two fluorine

environments. In the latter case the resonances were very close, indicating that there was little difference in the shielding of the two different types of fluorine. The differences in the two systems were said to arise because there could only be a limited d_π-p_π interaction in the d^{10} case, but in the d^o case these are three d orbitals of the correct symmetry for such an interaction with the p orbitals of the fluorine atom.

1.6.2. Titanium Tetrachloride and Tetrabromide

Titanium tetrachloride and tetrabromide are very similar in their chemistry. Virtually all the adducts of $TiBr_4$ are considered isostructural with those of $TiCl_4$. When $TiCl_4$ and $TiBr_4$ were mixed, Raman and mass spectroscopic evidence showed that the mixed halide compounds $TiCl_3Br$, $TiCl_2Br_2$ and $TiClBr_3$ were formed in the expected ratios for a random distribution of halide ions[26].

In this section the chlorides will be discussed in more detail since they are more relevant in the context of this work.

Titanium tetrachloride is a colourless liquid which can be distilled, without decomposition at 136°C. It fumes copiously in air and reacts vigorously with water.

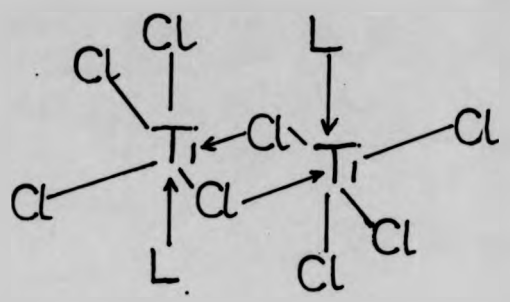
$$TiCl_4 \xrightarrow{H_2O} TiO_2(aq) + 4HCl$$

Consequently reactions of $TiCl_4$ must be carried out in a dry, inert atmosphere.

Titanium tetrachloride is the most studied of the tetrahalide derivatives, and in its reactions with the vast majority of ligands forms complexes where the titanium centre is in an octahedral environment irrespective of the stoicheiometry (1:1 or 1:2 with unidentate ligands, or 1:1 with most bidentate ligands) of the adduct.

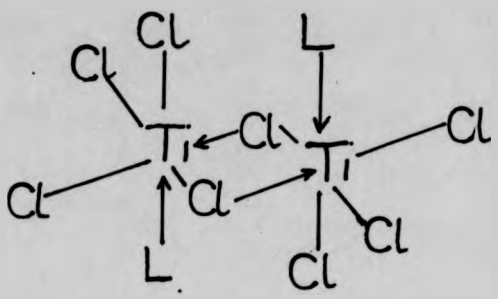
The stoicheiometry of an adduct is often governed by the conditions of its preparation. Hence the 1:1 and 1:2 adducts, $TiCl_4.POCl_3$ and $TiCl_4.2POCl_3$, were prepared by mixing $TiCl_4$ and $POCl_3$ in the appropriate molecular ratios, and melting the mixtures. On cooling single crystals of the respective adducts formed[27].

Several 1:1 adducts of the stoicheiometry $TiCl_4.L$ are formed with many donors (L). In all the examples where the structuresof these compounds have been established by X-ray methods, the complexes have been shown to contain octahedrally co-ordinated titanium. This is achieved by dimerization of the adduct by chloro-bridging [L = $POCl_3$ [28], EtOAc [29], $NCCH_2CO_2Et$ [30], $MeOC_6H_5CO_2Et$ [31], CH_3NO_2 [32]] as shown in the diagram below.



However, adducts with the 1:2 stoicheiometry, $TiCl_4.2L$ (or $TiCl_4.B$, where B is a bidentate ligand) are more common. Few of these have been structurally characterised, but those which have contain octahedrally co-ordinated titanium in simple monomers [L = $POCl_3$ [33], B = $CH_3CO.O.OCCH_3$ [34]]. More comprehensive lists of complexes have been well documented[7,11], as have more recent developments[12,13].

The structures of many adducts have been assigned on the basis of evidence from their infra-red spectra[35]. The number of Ti-Cl stretching bands observed in the region 200 - 450 cm^{-1} is diagnostic of the geometry of these complexes. Complexes in which the ligands are in a *cis* orientation to one another, such as $TiCl_4.2POCl_3$, possess C_{2v} symmetry, and therefore have three infra-red active Ti-Cl stretching modes, whereas complexes in which the ligands are *trans* to one another have D_{4h} symmetry, and therefore have only one infra-red active Ti-Cl stretching mode. However, analysis of the spectra is not always trivial as ligand bands may also occur in this region of the



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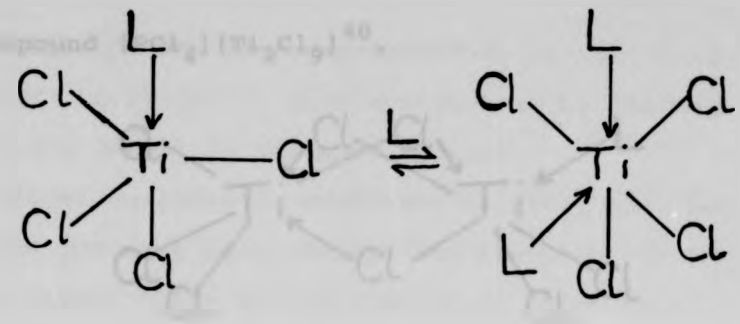
spectrum, and the Ti-Cl absorption bands may not be completely resolved.

The factors which affect the stoicheiometry of a complex, or indeed which geometry a complex adopts within that stoicheiometry, are not clearly understood.

Weak donors, such as esters[29,31], and CH_3NO_2,[32] form 1:1 adducts which are chloro-bridged dimers, whereas stronger donors form 1:2 monomeric adducts. On the other hand, several ligands, such as phosphines, and even some esters[36,37], form adducts of both types. As described above the adduct which is formed can merely be dependent on the ratio of the reactants in the reaction mixture, but there can be complicated equilibria in solution. A study involving $TiCl_4$ and PMe_2Ph, mixed in different ratios in CH_2Cl_2 solution has been made using ^1H and ^{31}P n.m.r. spectroscopy[38]. The results indicate that the 1:1 and 1:2 adducts are in equilibrium when the phosphine is present in excess. The monoadduct (1:1) can be isolated from a solution in which $TiCl_4$ is present in excess.

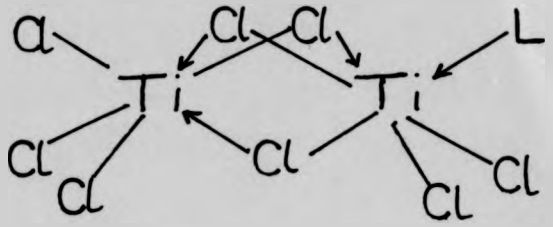
On the basis of molecular weight and infra-red evidence, the 1:1 adduct was assigned a monomeric structure rather than the more usual chloro-bridged dimeric structure.



The 1:2 adduct can be prepared by mixing the reactants in a CH_2Cl_2 solution with the phosphine in excess. This was assigned a *cis* structure on the basis that three bands at 415, 340 and 305 cm^{-1} in the infra-red spectrum could be assigned to Ti-Cl stretching modes.

Evidence was also found for the existence of another species in solution, formulated as $(TiCl_4)_2.PMe_2Ph$. This is discussed in detail in Chapter 4. Unfortunately the compound formulated as $(TiCl_4)_2.PMe_2Ph$ was not isolated, although a related complex has subsequently been characterised. The adduct $(TiCl_4)_2.HMPA$ [HMPA = $OP(NMe_2)_3$] is formed when the reactants are mixed in nitromethane with $TiCl_4$ in slight excess of a 2:1 ratio[39]. A confacial bioctahedral structure was proposed for the compound on the basis of infra-red evidence, where two Ti-Cl terminal (416, 379 cm^{-1}) and two Ti-Cl bridging stretches (268, 230 cm^{-1}) were assigned. This type of structure has been identified in the isoelectronic ion, $[(TiCl_4)_2Cl]^-$, in the

compound $[PCl_4][Ti_2Cl_9]$[40].



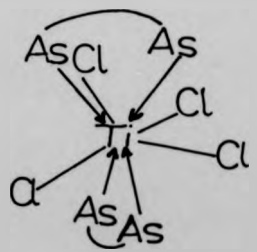
The HMPA was assigned to a terminal rather than a bridging position on the basis of evidence from ^{1}H, ^{13}C and ^{31}P n.m.r. spectroscopy. The resonances in the spectra of $(TiCl_4)_2$HMPA were close to those observed in the spectra of $TiCl_4 \cdot 2HMPA$, whereas a bridging ligand would be likely to give rise to signals which were significantly down-field of those observed due to deshielding effects.

Complexes of $TiCl_4$ with a co-ordination number other than six though rare do exist. The reaction of $TiCl_4$ with one mole equivalent of trimethylamine in benzene solution affords a 1:1 adduct, $TiCl_4.NMe_3$[41]. This was assigned a t.b.p. structure on the basis of evidence from infra-red and Raman spectra[42]. It was suggested that the large bulk of this ligand was the key factor in titanium adopting this co-ordination number and geometry.

Other ligands which form complexes of this type usually also form 1:2 adducts when the ligand is present in excess, as discussed above, but the further

reaction of NMe_3 is complicated by reduction of Ti(IV) to Ti(III). This system will be discussed in more detail in the next section.

Eight co-ordinate complexes of $TiCl_4$ have been known for some time, though few examples are known. The ligand DIARS [o-$C_6H_4(AsMe_2)_2$], which is a potentially bidentate donor through arsenic atoms, and its phosphorus analogue, both form eight co-ordinate dodecahedral complexes[43,44]. However, a very delicate balance of electronic and steric properties of the ligand is required to bring about this mode of co-ordination. The ethyl analogues of these ligands form only 1:1 adduct, for apparently steric reasons, while ethylene diarsine, $Me_2AsCH_2CH_2AsMe_2$ does not form a 1:2 adduct though it has no greater steric requirements than DIARS[45].



These complexes are not unique in titanium chemistry as $Ti(NO_3)_4$[46], and $Ti(S_2CNR_2)_4$[47], also show eight co-ordination around the metal centre.

1.6.3. Titanium Tetraiodide

Titanium tetraiodide is not a strong Lewis acid. Complexes (1:2) are formed with strong ligands such as pyridine, $TiI_4 \cdot 2py$, but the reactions of these compounds are often complicated as the reactants are degraded, and molecular iodine is produced. The products of these reactions, which are often of variable composition, can also be oxyiodides of titanium triiodide.

The triiodide, TiI_3, forms complexes which usually have the same stoicheiometry as $TiCl_3$ and $TiBr_3$ analogues[48]. It seems that TiI_3 resembles $TiCl_3$ much more closely than TiI_4 resembles $TiCl_4$ or $TiBr_4$, because of the reducing nature of iodide compared to the other halides. Thus iodide reduces Ti(IV) to Ti(III), but it is not a strong enough reducing agent to react further with Ti(III).

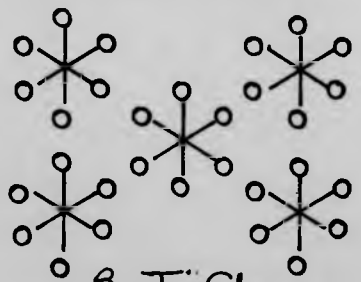
1.7. Co-ordination Chemistry of Titanium Trichloride

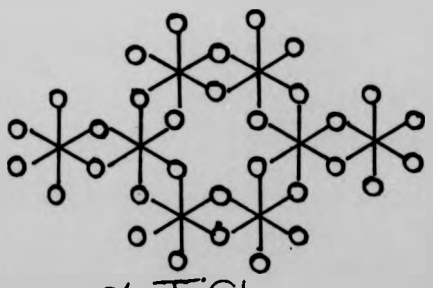
The co-ordination chemistry of $TiCl_3$ is also dominated by a co-ordination number of six for the titanium atom. This is demonstrated not only by the majority of the adducts of $TiCl_3$, but also in the structures of the different solid forms of $TiCl_3$.

There are four different crystalline modifications

of $TiCl_3$, namely α, β, γ, and δ[49]. β-$TiCl_3$ is produced by hydrogen reduction of $TiCl_4$, while heating this to 120°C yields γ-$TiCl_3$, and the α form is produced by further heating to 300-400°C. The δ form is produced by ball-milling the α or γ forms for prolonged periods.

The α, γ and δ forms of $TiCl_3$ all have layer structures of close packed anion planes, with titanium atom in two-thirds of the octahedral holes between every other plane. Unlike the other forms, β-$TiCl_3$ has a chain structure with titanium atoms stacked above each other between every anion plane. In all cases there is octahedral co-ordination of the titanium atoms.





Titanium trichloride forms adducts with a large number of ligands, usually by direct combination of $TiCl_3$ with the ligand, which produce a variety of formulations:

(i) $[TiL_6]^{3+}$

(ii) $[TiL_4Cl_2]^{+}$

(iii) TiL_3Cl_3

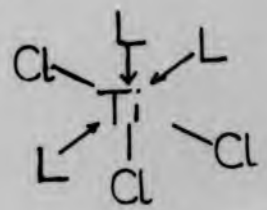
(iv) TiL_2Cl_3

Very few of these compounds have been structurally characterised by X-ray methods, so generally such compounds have been identified by techniques such as visible and infra-red spectroscopy, and the measurement of magnetic moment. The early work in this field has been reviewed by Coutts and Wailes[50].

Compounds of type (i) are formed when $TiCl_3$ is dissolved in strong ligands such as water[20] or urea[51]. This type of complex is easily identified by conductivity measurements, and identification of ionic chlorides by precipitation methods.

The alcohol complexes of $TiCl_3$ were originally formulated as type (i), but they are now known to be type (ii). The structure of the 1:4 iso-propanol adduct has been determined by X-ray methods, and it has been shown to possess a *cis* configuration as $[Ti(isopropanol)_4Cl_2]^+Cl^-$[52]. Spectroscopic evidence indicates that the other alcohol complexes have similar structures[53].

The adducts of other oxygen donor ligands such as THF, acetone, and dioxan, are of type (iii). The structure of the THF adduct, $TiCl_3(THF)_3$, determined by X-ray methods, has been shown to have a *mer* configuration[54].



The adduct of the tridentate ligand $MeOCH_2CH_2OCH_2CH_2OMe$ has been shown to have a *fac*-structure by X-ray methods[55].

Thus there is an interesting comparison between ligands in the series H_2O, ROH and R_2O. The structures of the $TiCl_3$ adducts vary in type from $[Ti(H_2O)_6]^{3+}$, to $[Ti(ROH)_4Cl_2]^+$ to $[Ti(R_2O)_3Cl_3]$.

Some complexes of type (iv) with the formulation TiL_2Cl_3 actually contain titanium which is six co-ordinate in the solid phase due to chloro-bridging. The observed magnetic exchange between neighbouring titanium atoms is evidence for this type of structure in the adducts of the sulphur bonded ligands Me_2S and THT[56].

However, sterically demanding ligands, such as NMe_3, produce monomeric five co-ordinate compounds which have t.b.p. geometry around the metal atom. The compounds $TiX_3 \cdot 2NMe_3$ (X = Cl, Br) can be prepared by direct combination of the trihalide with NMe_3[41], or by reduction of the tetrahalide with excess ligand. The structure of $TiBr_3 \cdot 2NMe_3$ was determined as t.b.p. by X-ray crystallography[57], and the $TiCl_3$ complex was assigned a similar structure on the basis of the comparison of the infra-red spectra of the two compounds. The bulk of the NMe_3 ligand is thought to be important in producing penta-co-ordination, as the corresponding dimethylamine adduct, $TiCl_3 \cdot 2NHMe_2$, is

dimeric and thus contains six co-ordinate titanium atoms.

It has also been observed that the five co-ordinate species, $TiCl_3 \cdot 2NMe_3$, reacts slowly to produce a binuclear species, $Ti_2Cl_6 \cdot 3NMe_3$, which probably contains octahedrally co-ordinated titanium atoms[58].

The trimethylamine adduct has been used in the preparation of other $TiCl_3$ adducts by displacement reactions. For example, the two NMe_3 ligands are readily replaced by other ligands such as dioxan, acetonitrile[59], and $N(CH_2CH_2NMe_2)_3$ [60].

Solutions of $TiCl_3$ in EtOAc have also been used in this role, but in this case one EtOAc ligand remains co-ordinated to $TiCl_3$ when three mole equivalents of nitrogen donor ligands, such as pyridine or aniline, are added to this solution. The isolated solids were formulated as $TiCl_3.2L.EtOAc$[61].

Thus $TiCl_3$ forms adducts with a very wide variety of ligands, and these adducts can have a series of different structures. To date there is no way of predicting unambiguously which type of complex a particular ligand will form, and it seems unlikely that definitive guidelines will be possible until many more adducts have been characterised.

1.8. Co-ordination Chemistry of $TiCl_2$

Addition compounds of titanium dichloride have

the general formula $TiCl_2.2L$ where the ligand, L, can be a nitrogen, oxygen or sulphur donor[62]. These compounds can be prepared by direct reaction of $TiCl_2$ with the ligand, but the reaction times are very long because the polymeric $TiCl_2$ dissolves only slowly in donor solvents.

The acetonitrile adduct, $TiCl_2 \cdot 2CH_3CN$ is significantly more stable than the other adducts, and displacement of this ligand has been used successfully as a method of preparation of other complexes e.g.

$$TiCl_2 \cdot 2CH_3CN \xrightarrow{L} TiCl_2 \cdot 2L + 2CH_3CN$$

(L = py, THF)

The trimethylamine adduct of $TiCl_2$, $TiCl_2 \cdot 3NMe_3$, was formed in low yields by reduction of $TiCl_3 \cdot 2NMe_3$ by the ligand itself[63], though another report suggests that when Na_2TiCl_4 was mixed with liquid NMe_3, the oxidation of Ti(II) to Ti(III) was accomplished by the solvent[62]. It would appear therefore that NMe_3 can act as both an oxidant and reductant, depending upon the reaction conditions.

On the basis of magnetic moment measurements the complexes of $TiCl_2$ were assigned a structure in which octahedrally co-ordinated titanium atoms were bridged by chlorides[62], though X-ray diffraction data is

required for a full characterisation of these compounds.

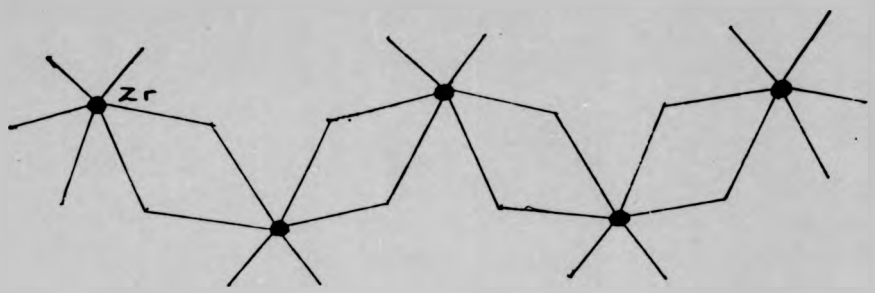
1.9. The Chemistry of Zirconium and Hafnium

The most striking feature of the chemistry of the two heavier members of Group IVA is their similarity. This is due to the closeness of the ionic radii of the M^{4+} ions (Zr, 0.74 and Hf 0.75Å), which is a result of the lanthanide contraction. However, due to the comparative rarity of hafnium, and difficulties in purifying the element, hafnium has been much less studied than zirconium. Differences between the elements may become more apparent as studies progress.

As with titanium there is an extensive chemistry of zirconium, and hafnium, in oxidation state (IV). The chemistry of these elements in oxidation state(III) is less well developed because of the strongly reducing nature of this state. For example there is no aqueous chemistry of Zr(III), because it is instantaneously oxidized to Zr(IV) by water.

The heavier congeners have a greater tendency than titanium to expand their inner co-ordination spheres, to form compounds in which the metal atoms have co-ordination numbers of six and above. Hence while $TiCl_4$ is monomeric with tetrahedral co-ordination

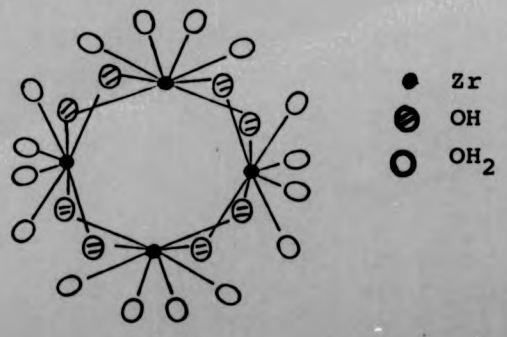
of the titanium atom, $ZrCl_4$, is a polymeric solid in which there is octahedral co-ordination of the zirconium atoms due to chloro-bridging[64].



1.10. Aqueous Chemistry of Zirconium

The aqueous chemistry of zirconium has been much more thoroughly studied than that of hafnium, and this discussion is therefore limited essentially to zirconium.

The zirconium species which crystallise from aqueous solution are polymeric, and contain eight co-ordinate zirconium atoms[65]. When $ZrCl_4$ is dissolved in water, and the solution concentrated, crystals of $ZrOCl_2.8H_2O$ precipitate. An X-ray study has shown that this contains tetrameric cations $[Zr(OH)_2(H_2O)_4]_4^{8+}$ [66].



(28)

The four zirconium atoms are linked by double hydroxy bridges in an eight membered ring.

The zirconium species found in solution vary greatly with the pH of the solution. The structures of these species are not known but evidence from techniques including light scattering, X-ray diffraction, and electromigration, suggest that trimers and tetramers are present. It was not clear if the zirconium atoms are oxo- or hydroxy-bridged, though this is probably pH dependent[67, 68].

1.11. Co-ordination Chemistry of $ZrCl_4$ and $HfCl_4$

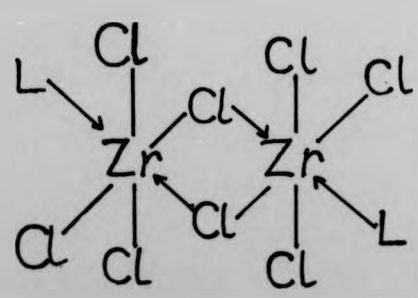
In this thesis some co-ordination chemistry of $ZrCl_4$ and $HfCl_4$ has been studied as a comparison for the analogous $TiCl_4$ systems. The well established co-ordination chemistry of the two compounds is briefly introduced here.

As discussed previously most investigations of these two elements have concentrated on zirconium, but when $HfCl_4$ co-ordination compounds have been studied, they have been found to be directly analogous to the corresponding zirconium adducts.

With most common ligands the behaviour of $ZrCl_4$ and $HfCl_4$ closely resembles that of $TiCl_4$. Thus they form simple monomeric complexes of the type $MCl_4 \cdot 2L$ in which the metal atoms are six co-ordinate (e.g. L = py, MeCN,

THF, Me_2S). Many of these have been described by Bradley and Thornton[69] and Larsen[70]. Infra-red evidence suggests that in most cases these complexes contain *cis* octahedrally co-ordinated metal atoms. This structure is more common with $ZrCl_4$ than with $TiCl_4$ because there is less steric interaction between bulky ligands co-ordinated to the larger zirconium metal centre.

Generally weak donors, such as EtOAc, also form 1:2 complexes with $ZrCl_4$, as opposed to the chloro-bridged 1:1 adducts which they form with $TiCl_4$. However, chloro-bridged 1:1 adducts of $ZrCl_4$, such as $(ZrCl_4.NCI)_2$ are becoming known[71]. This compound was assigned the structure shown below on the basis of a detailed analysis of its infra-red and Raman spectra.



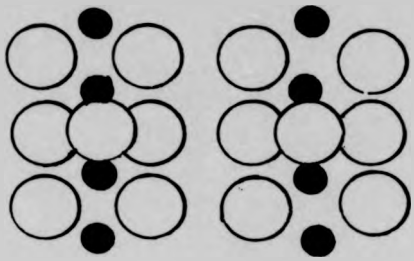
The $TiCl_4$ analogue was also assigned this structure, but no reasons were suggested as to why the ligand NCI should take up an equatorial position in the complex rather than the normal axial position[71].

The tendency to form eight co-ordinate complexes is even greater for $ZrCl_4$ and $HfCl_4$ than for $TiCl_4$. Thus

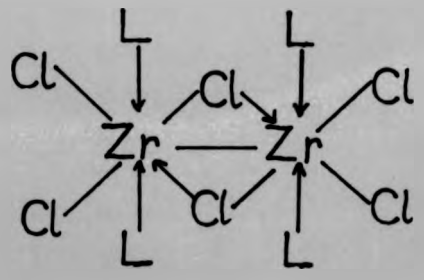
ligands which form complexes with co-ordination number eight with $TiCl_4$, such as DIARS, also form eight co-ordinate complexes with $ZrCl_4$ and $HfCl_4$[72]. Some ligands, which form six co-ordinate complexes with $TiCl_4$, form eight co-ordinate adducts with $ZrCl_4$. Examples include ligands such as DMPE[73], and compounds such as $(ZrCl_4)_2 \cdot 3bipy$ which has been tentatively assigned the formulation $[ZrCl_2(bipy)_3]^{2+}\ [ZrCl_6]^{2-}$, in which there are eight co-ordinate zirconium atoms in the cations, on the basis of evidence from infra-red spectra[74]. It is difficult to predict the geometries of these eight co-ordinate compounds, since examples of complexes with both dodecahedral and square antiprismatic geometries are known. There appears to be very little energy difference between these two geometries. For example, the anion $[ZrF_8]^{4-}$ has been shown to have a square antiprismatic geometry in the salt $[Cu(H_2O)_6]_2^{2+}\ [ZrF_8]^{4-}$ [75], and a dodecahedral geometry in the mixed salt $Li_6^+\ [BeF_4]^{2-}\ [ZrF_8]^{4-}$, as shown by X-ray diffraction methods[76].

1.12. Co-ordination Chemistry of $ZrCl_3$

Zirconium trichloride has an infinite chain structure in which $ZrCl_6$ octahedra share opposite faces[77]. The Zr-Zr bond distance of 3.07Å is consistent with the presence of some degree of metal-metal bonding.



Adducts of $ZrCl_3$ with nitrogen donor ligands have been prepared by prolonged reaction with the ligand, or by precipitation of the adduct from an acetonitrile solution of $ZrCl_3$ [78]. The adducts have a variety of formulations, such as $ZrCl_3 \cdot 2py$, $(ZrCl_3)_2 \cdot 5CH_3CN$, $(ZrCl_3)_2 \cdot 3bipy$, and $(ZrCl_3) \cdot 3phen$. Each of these compounds has been consigned a different structure on the basis of evidence from conductivity measurements, magnetic moments measurements, and infra-red spectroscopy. The pyridine complex has been suggested to be a chloro-bridged dimer with axial ligands, on the basis that the measured magnetic moment was low for Zr(III), and this structure has been confirmed for the compound $[ZrCl_3(PBu_3)_2]_2$ by X-ray diffraction methods[79].



The metal-metal distance in this compound is 3.18Å, which is consistent with the presence of some degree of metal-metal bonding.

This compound, together with the PEt_3 and PPr^n_3 analogues, have been prepared by the reduction of the corresponding $ZrCl_4$ adducts, using a stoicheiometric amount of sodium amalgam in benzene solution[79].

The reactions of $ZrCl_3$ with lutidine ligands have been shown to be more complex, and so involve oxidation-reduction reactions. The products recovered possess a very similar X-ray diffraction pattern to the $ZrCl_4$ adducts of the ligands. This evidence, combined with magnetic susceptibility measurements, has led to the proposal that the products are a mixture of Zr(III) and Zr(IV) species[80].

1.13. Co-ordination Chemistry of Tin Tetrachloride

In the course of this work some co-ordination chemistry of $SnCl_4$ has been studied, because in many ways it is similar to that of $TiCl_4$. There are obvious similarities between $SnCl_4$ and $TiCl_4$. Tin tetrachloride like titanium tetrachloride is a colourless liquid at room temperature which fumes in air, and reacts vigorously with water. Both compounds contain tetrahedrally co-ordinated metal atoms.

There are similarities in the co-ordination

chemistries of $TiCl_4$ and $SnCl_4$, in that both are strong Lewis acids which react with a wide range of ligand molecules to form complexes in which there is octahedral co-ordination of the metal. The majority of the complexes of $SnCl_4$ are of the type $SnCl_4 \cdot 2L$[81].

The *cis* and *trans* isomers of several adducts of the type $SnCl_4 \cdot 2L$ have been shown to be in an equilibrium, which is dependent on solvent polarity, by Raman and n.m.r. spectroscopy[82,83]. It is possible to isolate the *cis* isomers from CH_2Cl_2 solution, and the *trans* isomers from pentane solution. When the adducts $SnCl_4 \cdot 2L$ (L = DMF, DMA, DMSO) were initially isolated from a range of organic solvents, they were assigned a *cis* structure on the basis of their infra-red and Raman spectra[84]. It was found that on standing at room temperature for several months, or heating for thirty minutes, the adducts isomerized to the *trans* form. These observations were rationalized on the basis that the *cis* isomer is preferred in solution on electronic grounds, but in the solid state ligand interactions, which may be inter- or intra-molecular, render the *trans* isomer the more favoured.

It is not simple to rationalize the observations described above. Zahrobsky[85] has proposed a stereo-chemical model based on the consideration of non-bonding interactions of ligands in MA_4B_2 systems. This model

predicates that all such systems, including those of the type $SnCl_4 \cdot 2L$ should have a *cis* configuration, regardless of the relative sizes of the donor atoms.

Other explanations of the geometry of $SnCl_4 \cdot 2L$ complexes based on the nature of Sn-Cl and Sn-L bonds, and their effect on the energy of the tin atomic orbitals, have been proposed by Smith and Wilkins[86], and developed by Drago *et al*[87]. If two low polarity Sn-L bonds are formed, as in cases where L is a strong donor, then the d-orbitals of Sn(IV) are too high in energy to be used in bonding, and *trans* Sn-L bonds are formed using an sp_z hydrid orbital.

If the ligands, L, are of comparable electronegativity to Cl then sp^3d^2 hydrization becomes possible, and the molecule adopts a *cis* configuration, as this minimizes the splitting between the $d_{x^2-y^2}$ and d_{z^2} orbitals.

CHAPTER 2

2.0. Introduction to Ziegler-Natta Catalysts

The discovery that mixtures of a transition metal compound, and an organometallic compound of a main group element, facilitate the low pressure polymerization of ethylene was made by Ziegler and his co-workers in 1953[88]. Until then ethylene could only be polymerized using a free-radical catalyst at high temperatures (150-230°C), and high pressures (1000 - 3000 atm.), using process discovered by I.C.I. PLC, and developed during the Second World War.

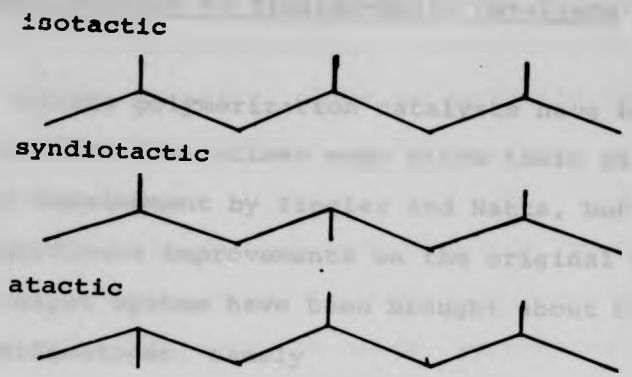
It was quickly established that the most active catalyst was a mixture of an aluminium alkyl and titanium tetrachloride, though all the elements in Groups IVA, VA and VIA were very active in this respect.

There was great industrial interest in this discovery because of the mild conditions required to bring about polymerization, and also because the polyethylene produced by this method was different to that produced by the radical process. Polyethylene made by the radical process is highly branched, in a random manner, so the solid product is amorphous. Branches are almost entirely absent from the polymer made using a transition metal catalyst. As a consequence of this regular, long-chain, structure, polyethylene made with a Ziegler-type catalyst can crystallize in a lamellar form. Hence it has different physical properties from

polyethylene produced by the radical process, including a higher density, and a higher melting point.

The titanium based catalyst was found to be versatile, in that in contrast to the radical process, it could bring about the polymerization of dienes, α-alkenes, such as propylene and the co-polymerization of two different alkenes. The polymerization of propylene was investigated by Natta and his co-workers, under an agreement which Ziegler had with the Italian company Montedison Spa. Natta discovered that propylene was polymerized to a mixture of crystalline and amorphous solids, and that the proportion of crystalline product could be increased by using $TiCl_3$ in the catalyst preparation rather than $TiCl_4$[89,90]. The structure of the crystalline polypropylene which Natta called isotactic, was investigated by X-ray diffraction techniques. It was found to be a stereoregular polymer in which propylene monomers were linked in a head-to-tail manner, to form a long chain helix in which all the methyl groups were on the same side of the carbon back-bone. The amorphous product was called atactic, and this has a structure in which the methyl groups are randomly arranged on either side of the carbon back-bone, as shown below.

Syndiotactic polypropylene, which is produced by some vanadium catalysts[91], has alternate methyl groups on different sides of the carbon back-bone.



Most catalysts produce a mixture of isotactic and atactic polypropylene, but to be commercially viable a catalyst must produce a high proportion (> 95%) of isotactic polymer. It is this form which has the industrially attractive properties of a high melting point (165-170^{o}C), high tensile strength, hardness, and low density, though it is brittle compared to polyethylene.

The diversity in the possible products of propylene polymerization makes the specification for an industrially useful catalyst very stringent. This has inspired a large amount of industrial research into producing catalysts with high polymerization activity which produce high proportions of stereoregular polypropylene. It is well recognised commercially that while it is relatively easy to polymerize ethylene the requirements to produce an effective polymerization catalyst for propylene are much more demanding.

2.1. Modifications to Ziegler-Natta Catalysts

Alkene polymerization catalysts have been modified in countless ways since their discovery and development by Ziegler and Natta, but the most significant improvements on the original $TiCl_4/AlR_3$ catalyst system have been brought about by two modifications, namely

(i) the addition of ligands to the catalyst[92]

(ii) supporting the titanium compound on a high surface area material[93].

These modifications have led to improvements in both the activity and stereoselectivity of the catalysts. The role of both the ligands, and the supporting material, is as yet not well defined.

Common ligands sited in patents are amines, phosphines, ethers, alcohols and esters[5], though many different ligands have been investigated in this context.

Addition of ligands to catalyst preparations is particularly important in the production of stereo-regular polypropylene, so the ligand may have a role in orientating the monomer during the polymerization reaction, or the ligand may block sites which produce irregular polymer.

The motivation for supporting the titanium compound was that, as the catalysts are at present essentially

heterogeneous, only the surface of the solids are active in polymerization. Therefore much of the potential activity, which is currently believed to be associated with the titanium atoms, is not being used.

Supporting the ethylene catalyst proved straightforward, and a range of materials, such as silica, alumina, and magnesium oxide, were found to be successful in this role. However, with propylene the extra criterion of stereoregularity in the product made catalyst specifications considerably more stringent.

The most widely used and successful support material for propylene polymerization catalysts has proved to be anhydrous magnesium chloride, and even with this material the catalyst preparation has to follow a well defined sequence to obtain the best results. One procedure used to prepare a commercially used catalyst is detailed in the scheme below[92].

$7MgCl_2$: 1EtOBz
ball mill 100 hours, 40°C

↓

add $TiCl_4$ (15g per g $MgCl_2$/EtOBz)
2 hours, 80°C

↓

filter hot, wash
twice with hexane

↓

treat with $AlEt_3$/EtOBz

↓

add C_3H_6, form isotactic
polypropylene

This procedure produces a very high surface area catalyst, which has a surface monolayer of titanium. The initial ball-milling with the ligand is believed to break up the $MgCl_2$ lattice, because the X-ray spectrum of the product is diffuse, and different from that of the original $MgCl_2$[5]. Treatment with $TiCl_4$ then removes much of the ligand, and the titanium becomes intimately adsorbed into, or bonded onto, the support.

The high activity of $MgCl_2$-supported catalysts has been attributed to an increase in the rate of propagation[94], and an increase in the number of active sites[95], in comparison with unsupported catalysts which are usually based on solid $TiCl_3$.

Two reasons have been suggested as to why $MgCl_2$ is so unique in this system[5]. Firstly, Mg^{2+} and Ti^{4+} ions have similar ionic radii (0.68 and 0.65Å respectively), and so they could be compatible in the same lattice. Secondly, the structure of $MgCl_2$ is a layer lattice with cubic close-packed chloride anions, which is the same as that of γ-$TiCl_3$, and similar to that of α-$TiCl_3$, which has hexagonal close packing. This may be significant, as some titanium will undoubtedly be present as Ti(III) after reaction with the aluminium alkyl.

It has not been established why aromatic esters, such as ethyl benzoate, are among the most effective

ligands for the stereospecific polymerization of propylene with $MgCl_2$-based catalysts. Other esters have been used, but the benzoate is frequently the ligand used in catalysts prepared by the ball-milling technique.

Catalysts of this type are very effective in propylene polymerization, a typical activity being 16 kg of polymer produced per millimole of titanium in the catalyst. The very high activities are necessary because there is a large commercial advantage in not having to separate the catalyst residues from the polymer product. The catalysts are believed to lose activity because the large amount of polymer they produce inhibits the access of the monomer to the active centres.

An industrially used catalyst will leave as little as 3 p.p.m. titanium in the polymer, but as titanium is such a small part of the supported catalyst this means there could be as much as 100 p.p.m. chloride. To be successfully marketed polypropylene must have as low a chloride content as possible, as residual chloride in the polymer accelerates the corrosion of fabricating machinery. This has led to a large current interest in reducing the chloride levels in catalysts either by using support systems other than magnesium chloride, or by using different titanium compounds. Derivatives such as the hydroxide,

alkoxides or carboxylates have been considered[96,97], and the carboxylate compounds in particular are referred to later in Chapter 3.

Since the active constituent of the catalyst, titanium, is present at a much lower level than the support material, it is very difficult to study these systems by conventional chemical and spectroscopic techniques. Also they are inhomogeneous systems, in that titanium can be present in many different environments, only some of which are active catalytic centres. Modern techniques which are currently being applied in this area include solid state N.M.R., E.X.A.F.S. (Extended X-ray Absorption Fine Structure), S.I.M.S. (Secondary Ion Mass Spectrometry), and Fourier Transform I.R. Spectroscopy.

2.2. Studies of Catalysts

Several experiments have been devised in an attempt to clarify, and estimate the role played by titanium centres in the catalyst.

Boor has studied the effect of nitrogen donor ligands on an unsupported $TiCl_3$ catalyst system[98]. He observed that when a low donor: $TiCl_3$ ratio was used, the proportion of monomer converted to polymer was decreased, but the polymer was more stereoregular. Boor rationalized this by proposing that the titanium

centres which did not produce stereoregular polymer were strong acceptors, and were thus preferentially complexed and deactivated. As more ligand was added to the catalyst preparation the activity increased. It was suggested therefore that either the electron donors could become absorbed on the surface of the catalyst, and possibly enhance its activity, or more likely that the ligand could break up the catalyst particles exposing more catalytic centres. The latter proposal was supported by evidence from electron microscopy studies[99], where catalyst particle sizes were shown to decrease on addition of electron donors.

A further, and possibly complementary, explanation arises from the formation of $AlEtCl_2$ by the reaction:

$$TiCl_3 + AlEt_2Cl \rightarrow TiCl_2Et + AlEtCl_2$$

Caunt has suggested that since $AlEtCl_2$ is a known catalyst poison, in that when it is added the activity of the catalyst is lowered, the ligands complex with, and remove, this poison, thus making the catalyst more active[100].

Chien and co-workers have studied one particular $MgCl_2$ supported catalyst, in which *p*-cresol was added to the usual ball-milled mixture of $MgCl_2$, $TiCl_4$, and EtOBz. The catalyst precursor was activated with triethyl aluminium and it was determined that the Ti(IV)

was reduced to Ti(III) and Ti(II). They devised a useful method for determining the ratio of reduced states present, by titration against solutions of iron(III) sulphate and sulphuric acid[101].

In the presence of molar sulphuric acid Ti(II) is oxidized to Ti(III), which can be titrated against Fe(III)

$$Ti^{2+} + H^{+} \rightarrow Ti^{3+} + \tfrac{1}{2}H_2 \quad (1)$$

$$Ti^{3+} + Fe^{3+} \rightarrow Ti^{4+} + Fe^{2+} \quad (2)$$

This reaction does not take place in neutral solution so that under these conditions both the Ti(II) and Ti(III) present can react with Fe(III).

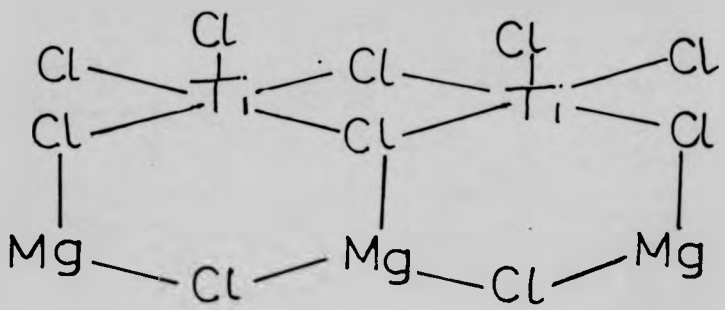
$$Ti^{2+} + 2Fe^{3+} \rightarrow Ti^{4+} + 2Fe^{2+} \quad (3)$$

$$Ti^{3+} + Fe^{3+} \rightarrow Ti^{4+} + Fe^{2+} \quad (4)$$

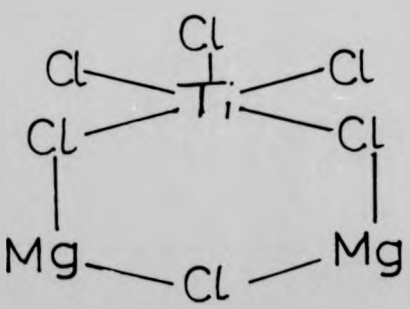
The amount of Fe(II) produced can be calculated from a back titration with dichromate. Hence the total reducing power of the catalyst could be deduced from equations (3) and (4), the fraction of Ti(II) being the difference calculated from the two titrations.

They also observed two different signals in the E.S.R. spectrum of the activated catalyst corresponding to Ti(III) centres, but determined that only 20% of the Ti(III) present gave a signal, so that 80% was "E.S.R. silent"[102].

The E.S.R. active centres were suggested to be $TiCl_3$ species bridged to surface chlorides in two different ways to make the titanium atoms five co-ordinate.



The Ti(III) centres which gave no E.S.R. signal were proposed to be chloro-bridged dimers, which could be dipolar coupled, so that lines in the E.S.R. spectrum become too broad to be observed.



It is both interesting and relevant that no evidence for ester co-ordination to titanium was found. In particular evidence from infra-red (i.r.) spectroscopy

showed that the bands observed in the carbonyl stretching region (1750-1550 cm^{-1}) of the spectrum of a $TiCl_4$/EtOBz catalyst supported on $MgCl_2$, occurred in the same region as those found in the system when $TiCl_4$ was absent[103].

Recently even more sophisticated $MgCl_2$-supported catalyst systems have been investigated. In the polymerization of the optically active alkene, 4-methyl-1-hexene, in the presence of the optically active Lewis base, methyl anisate, stereoselectivity in the synthesis of regular polymers was very high, and enhanced by the presence of the ligand. This was determined by optical rotation measurements on the fractions of the polymer which were soluble in various solvents, including EtOAc, Et_2O, and C_6H_6[104].

The conclusion was drawn that the catalytic system was able to distinguish between the two antipodes of the monomer, which were polymerized at slightly different rates at catalytic centres of different chirality, because a racemic monomer was polymerized to an optically active polymer.

Another interesting, and possibly significant, development has been reported very recently. Japanese workers have studied the polymerization of ethylene by an aluminium alkyl supported on $MgCl_2$, in the absence of any transition metal compounds[105]. It was reported that a high molecular weight polymer was

produced by this system. This observation led to the proposal that aluminium centres were the polymerization sites in conventional Ziegler-Natta catalysts, and that metal halides, such as $MgCl_2$, markedly increased the propagation rate. It should be noted that the yield of polymer was very low, and it has been known since the early work of Ziegler that aluminium alkyls react with ethylene to produce oligomers. This new evidence has still to be substantiated, the possibility of trace quantities of transition metal ions being present must be eliminated, and the yield of polymer increased.

If aluminium is the site of polymerization rather than titanium, as is generally accepted, then titanium must have a fundamental affect on the system as titanium is required in the very active, commercially used catalysts, even though its precise role has still to be defined.

2.3. Mechanisms for Ziegler-Natta Polymerization

Early proposals for the mechanism of the polymerization of alkenes by $TiCl_4/AlR_3$ mixtures considered that alkyl radicals, or anions, formed according to the equations below, were chain initiators[106,107].

$$R_3Al + TiCl_4 \rightarrow R_2AlCl + RTiCl_3$$

$$RTiCl_3 \rightarrow R^{\bullet} + TiCl_3$$

$$R^{\bullet} + C_2H_4 \rightarrow R - CH_2 - CH_2 \text{ etc}$$

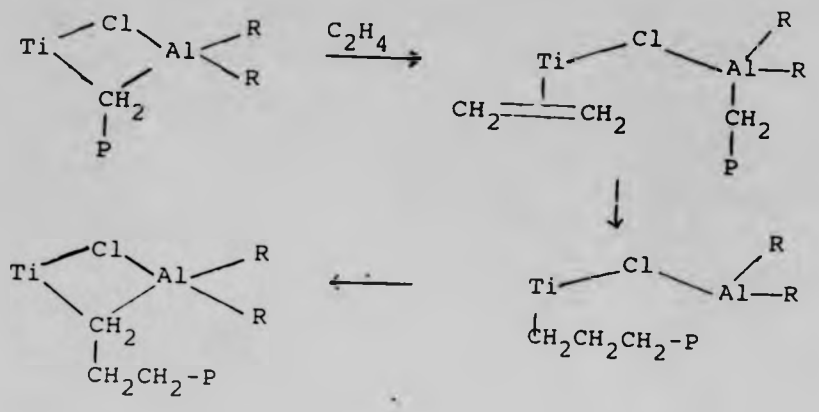
$$RTiCl_3 \rightarrow R^{-} + TiCl_3^{+}$$

$$R^{-} + C_2H_4 \rightarrow R - CH_2 - CH_2^{-} \text{ etc}$$

However it is now generally believed that polymerization takes place while the polymer chain is co-ordinated to a metal centre, but it is a matter of some debate whether the site of co-ordination is titanium, aluminium, or both metals.

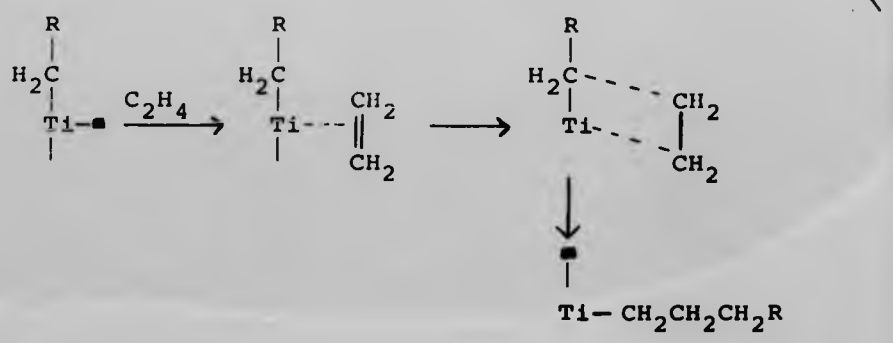
It is known from the early work of Ziegler's group, that oligomers form in the reaction of ethylene with aluminium alkyls, so chain growth at this metal centre was suggested on the basis of this evidence. However, it is likely that titanium has an important role in the polymerization reaction, as polymerization by $TiCl_4/AlR_3$ mixtures produces a much higher molecular weight polymer than AlR_3 alone.

Natta[108] suggested that the polymer chain bridged between titanium and aluminium and ethylene was activated by co-ordination to titanium.



The observation that titanium alkyl compounds (such as $MeTiCl_3$) catalyse the polymerization of ethylene in the absence of aluminium compounds suggests that titanium is the site of reaction.

The most widely accepted mechanism for polymerization at titanium is due to Cossee and Arlman[109]. They consider that the aluminium alkyl reacts with the titanium halide to form a titanium alkyl. Ethylene is then thought to co-ordinate to titanium, and to react with the alkyl group through a four-centred cyclic intermediate.

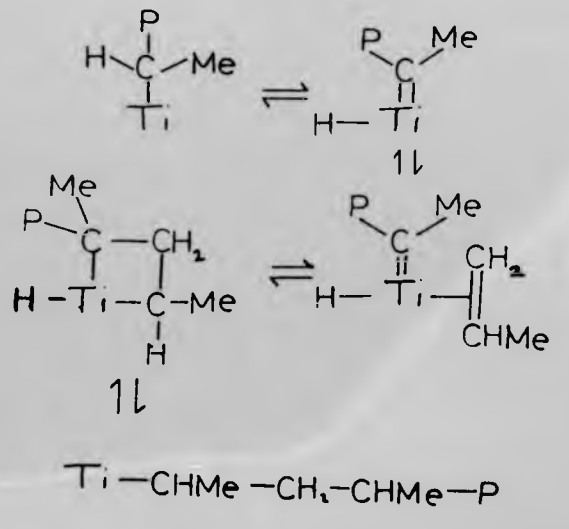


■ vacant site

The final step is required to explain the formation of stereoregular polymers with α-alkenes such as propylene.

Rodriquez and Van Looy[110] proposed a mechanism which is effectively a hybrid of the mechanisms suggested by Natta, and Cossee and Arlman, in which the polymer bridges between titanium and aluminium.

All these mechanisms consider that polymer chain growth occurs by 'insertion' of an alkene into a titanium alkyl bond, but a mechanism involving a titanium carbene has been suggested by Green and Rooney *et al*[111]. An α-elimination reaction from a titanium alkyl bond forms a hydride and a carbene. The carbene can then react with a co-ordinated alkene to form a metallocyclobutane intermediate, and hydride transfer from titanium to carbon completes the sequence. This mechanism is consistent with stereoregular polymerization of α-alkenes.



However all the proposals described above are speculative to the extent that the structure of the catalytic centre is not known. However, it is generally accepted that titanium is central to these reactions, so the study of its organometallic co-ordination chemistry may provide evidence which will help to distinguish between the various mechanisms.

2.4. Studies of the Components of Catalysts

In view of the difficulties associated with studying supported catalysts, investigations of model systems, which still show catalytic activity, may provide unambiguous and useful information.

This Chapter describes the preparation of compounds containing the basic catalyst components (i.e. $TiCl_4$, $MgCl_2$, and ligand), or related compounds (e.g. $ZrCl_4$, $HfCl_4$), as model systems.

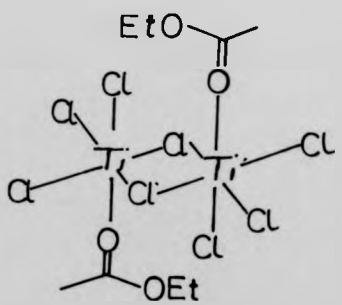
There has been very little information published on such systems. A few claims have been made in the patent literature, but this work has shown some of these claims to be invalid. This will be discussed further in Section 2.6.5.

First reactions between esters and either $TiCl_4$ or $MgCl_2$ will be discussed briefly, and then the known information on systems containing all three components will be presented.

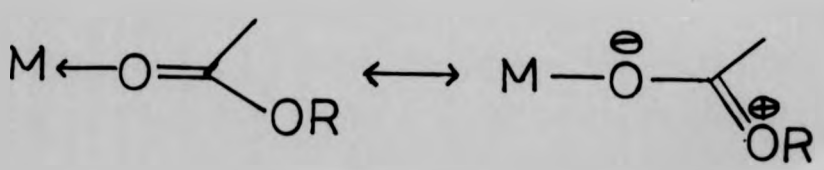
2.4.1. $TiCl_4$-Ester Adducts

Ester(L) adducts of $TiCl_4$ with the formulations $TiCl_4 \cdot 2L$, $(TiCl_4 \cdot L)_2$, and $(TiCl_4)_2 \cdot L$ have all been reported[7].

The 1:1 adducts have been best characterised by X-ray methods. The complexes with EtOAc[29] and $EtOOCC_6H_4OMe$[31], were found to be very nearly isostructural. As shown below the complexes are dimeric, and a co-ordination number of six for the titanium atoms is achieved by chloro-bridging.



The carbon-oxygen bond lengths of the carbonyl group are longer in the adducts than the free esters, and the carbon-oxygen bond lengths of the acyl linkages are correspondingly shorter. This is consistent with the view of bonding shown below.



These compounds, and the mono-adducts of other esters, can be prepared by mixing $TiCl_4$ and the appropriate ester in a stoicheiometric ratio in solvents such as benzene or petroleum ether.

The i.r. spectra of the mono-adducts are consistent with co-ordination via the carbonyl group of the esters. This has been inferred because the stretching frequency of the carbonyl group [ν(C=O)] is lowered on co-ordination, whereas the corresponding stretching frequency of the acyl group is increased.

The lowering of the carbonyl stretching frequency of EtOAc, [ν(C=O)], has been interpreted by Lappert[112] in terms of the relative Lewis acidities of metal halides. He reported that the [ν(C=O)] of EtOAc is lowered by 128 cm^{-1} on co-ordination to $TiCl_4$.

These studies, and others with phenyl acetate[113], are consistent with the view of bonding suggested by X-ray structure determinations, shown above.

Solid adducts of the type $TiCl_4 \cdot 2L$ have been reported to precipitate from solutions of $TiCl_4$ in esters of long chain carboxylic acids, such as ethyl stearate[37,114]. It should be noted, however, that it is not possible to prepare the bis-adducts of esters such as EtOAc by this method. In this work it was shown that removal of solvent from a solution of $TiCl_4$ in EtOAc yields a viscous oil, and heating this in *vacuo* in order to remove further solvent,

produces only the sublimation of the mono-adduct, $(TiCl_4 \cdot EtOAc)_2$.

Adducts with the formulation $(TiCl_4)_2 \cdot L$ (e.g. L = *n*-octyl acetate) have been reported to precipitate from solutions of the ester in excess $TiCl_4$[37,114]. No structure has been proposed for these adducts, but they presumably have the bridged structure as proposed for the HMPA adduct (Section 1.6.2.)[39]; namely that of a confacial bioctahedron, with a ligand occupying a terminal position.

Conductivity measurements on ester adducts of $TiCl_4$ have suggested that these compounds dissociate into ions, to a small extent, in chlorinated solvents[115].

$$(TiCl_4 \cdot L)_2 \rightleftharpoons TiCl_5 \cdot L^- + TiCl_3 \cdot L^+$$

The equilibria very much favour the non-ionised form. These results should probably be verified because small traces of water in the solution would produce similar results.

2.4.2. $MgCl_2$·-Ester Adducts

An unstable ethyl acetate solvate of $MgCl_2$ has been reported as $MgCl_2 \cdot 2EtOAc$[116]. The conductivities of solutions of this species were explained by the equilibrium:

$$MgCl_2 \cdot 2CH_3COOEt \rightleftharpoons 2CH_3CO^+ + [MgCl_2(OEt)_2]^{2-}$$

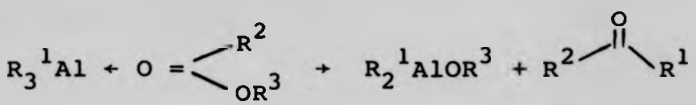
This system was the subject of preliminary studies to this work in the laboratories of I.C.I. PLC[117], where it was found that anhydrous $MgCl_2$ would dissolve in dry EtOAc. In this work it has been found that these solutions are saturated at about 0.5M, and that the solid isolated from such a solution, which is initially crystalline, loses EtOAc easily in *vacuo*, or on heating. The composition of the solid when freshly isolated is close to $MgCl_2 \cdot 2.75$ EtOAc, and the ester is lost gradually up to a temperature of 250°C, when only $MgCl_2$ remains. No well defined plateaux were observed during thermogravimetric analysis of this solid, indicating that there are no stable phases of solvated $MgCl_2$.

The ethyl benzoate solvate of $MgCl_2$ has been studied, because of the importance of this system as a support for polypropylene polymerization catalysts[118]. As anhydrous $MgCl_2$ is totally insoluble in EtOBz ball-milling techniques have to be used in the preparation of catalyst supports. The solvate formed by ball-milling $MgCl_2$ with an excess of EtOBz, and then washing with hexane, has compositions which vary between $MgCl_2 \cdot x$EtOBz (x = 0.1-2.0) depending on the time of reaction. The final product is $MgCl_2 \cdot 2.0$EtOBz, even after extended periods of ball-milling.

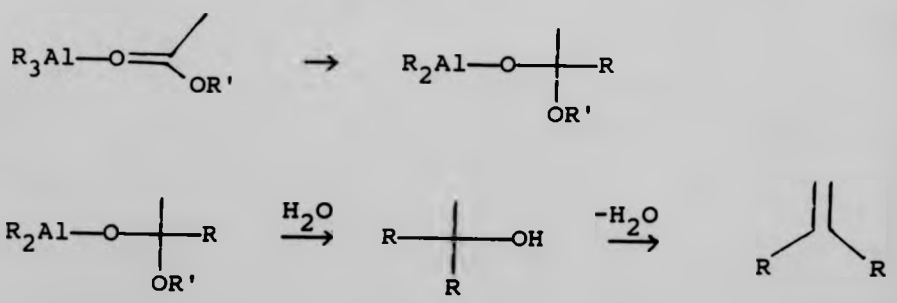
2.4.3. AlR_3-Ester Reactions

The reactions between aluminium alkyls (designated as AlR_3 for simplicity) and esters are complex, but have recently been studied in some detail[119, 120]. At low temperatures a 1:1 complex is formed initially, in which i.r. evidence suggests the ester is co-ordinated to aluminium through the oxygen of its carbonyl group.

On standing alkylation of the ester takes place and a ketone is formed.



Further alkylation produces alcohols, which generally dehydrate on aqueous work-up to give unsaturated final products.



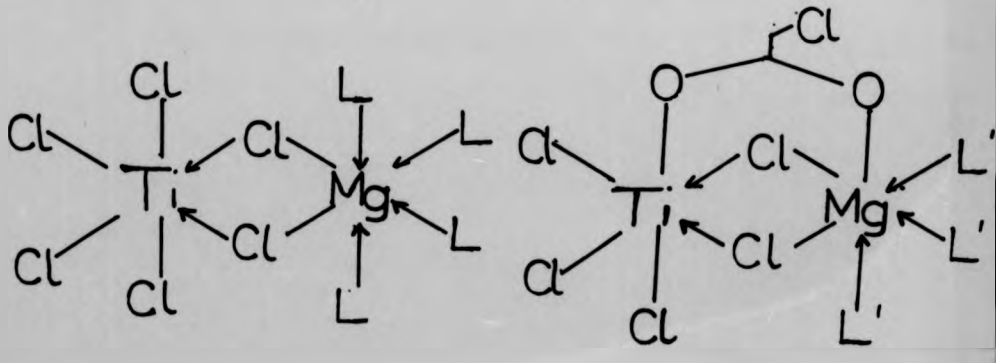
It is interesting to note that the esters of aromatic carboxylic acids, which are the esters of

choice in propylene polymerization catalysts are attacked only slowly by aluminium alkyls.

These systems have not been studied further in this work.

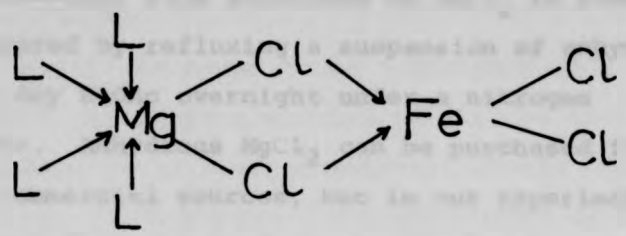
2.4.4. $TiCl_4$:$MgCl_2$:EtOAc systems

A patent to the Italian company Montedison Spa described materials prepared by mixing $MgCl_2$ and transition metal halides (including $TiCl_4$, $TiCl_3$ and VCl_3) in stoicheiometric ratios in EtOAc solutions[121]. These materials were not characterised other than by their proposed general formulations, and their ability to polymerize ethylene. Subsequently the crystal structure of one of the types of compound claimed in the patent, $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$, was published in the "open" literature[122]. Later the structure of a related compound, $MgCl_2 \cdot TiCl_3(O_2CCH_2Cl) \cdot 3EtO_2CCH_2Cl$, which was prepared by the reaction of $MgCl_2$ and $TiCl_4$ in ethyl chloroacetate solution, was also reported[123].



The structure of the compound $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$ was shown to be an edge-shared bioctahedron. There was octahedral co-ordination around both metal centres, and two chlorides bridged the two metals, (and thus formed the shared edge). The four EtOAc ligands completed the co-ordination sphere of magnesium, while four chlorides completed that of titanium. The compound could be viewed as a bis-adduct of $TiCl_4$ with *cis* geometry, in which the $(EtOAc)_4MgCl_2$ unit acted as a bidentate ligand. The formation and structure of the carboxylate bridged compound, $MgCl_2 \cdot TiCl_3(O_2CCH_2Cl) \cdot 3EtO_2CCH_2Cl$, are discussed in more detail in Chapter 3.

More recently another example of a compound in which an L_4MgCl_2 unit bridges to a transition metal halide has been reported[124]. The compound $MgCl_2 \cdot FeCl_2 \cdot 4THF$ was prepared by mixing $MgCl_2$ and $FeCl_3$ in a 1:1 ratio in THF as the solvent. Initially the ionic compound $(THF)_5MgCl \cdot FeCl_4$ was formed, but the Fe(III) was reduced to Fe(II) by decomposition of THF on standing, and crystals of $MgCl_2 \cdot FeCl_2 \cdot 4THF$ were isolated. The structure of the complex was determined by X-ray methods, which showed that while co-ordination around the magnesium atom was similar to that found in $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$, the L_4MgCl_2 unit bridged to a tetrahedral Fe(II) centre rather than an octahedral Ti(IV) metal centre.



2.5. Objectives of the work in this Chapter

In the light of the above discussion it was the aim of this work to prepare and to characterise more fully complexes involving $MgCl_2/MCl_4$/ligand, components (where M = Group IVA elements, or related elements). It was hoped to extend the series of compounds by varying the metal, M, and the ligand, and to determine their stabilities and solution properties, in order to compare them with the ill-defined solids prepared by ball-milling techniques. The lability of ester ligands in the solid phase and solution would be of particular interest, as their properties when part of a catalyst are not well understood, and they clearly play an important role in the formation of stereo-regular polymers.

2.6.1. Results and Discussion

Approximately 0.5M solutions of $MgCl_2$ in EtOAc were prepared by refluxing a suspension of anhydrous $MgCl_2$ in dry EtOAc overnight under a nitrogen atmosphere. Anhydrous $MgCl_2$ can be purchased from several commercial sources, but in our experience such material always contains small, but detectable (i.r. spectroscopy), amounts of water. The samples used in this work were supplied by I.C.I. PLC, and were essentially free of water. It was stored in a tightly sealed container, which was specially designed such that samples could be removed using Schlenk techniques, without exposure to any atmosphere other than dry nitrogen or argon.

The compound $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$, (I), was prepared by adding $TiCl_4$ dropwise, to a stirred ice-cooled solution of $MgCl_2$ in EtOAc, so that the molar ratio of titanium to magnesium was 1:1. The resulting yellow solution was then heated to 60°C for four hours, and on cooling the volume of the solvent was reduced by pumping until a yellow precipitate formed. The supernatant was removed from the solid by syringe, the solid was washed with petroleum ether, and dried in *vacuo* until the amorphous yellow powder was free flowing.

A crystalline product could be prepared by re-

dissolving (I) in a minimum volume of EtOAc, and allowing the solution to stand at room temperature for several weeks.

Compound (I) was found to be hydrolysed to a white powder within five minutes in air, so it had to be handled in an inert atmosphere at all times.

When 5.0g, (7.85 mmol) of (I) was heated to 80°C under reduced pressure (0.1 mm Hg) the weight loss measurements (1.40g, 28%) indicated that two moles of ligand (calcd. wt. loss 1.38g) were lost, and the pale yellow solid residue analysed as $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc$. It was often difficult to collect two moles of free EtOAc absolutely quantitatively, but the liquid (approx. 2 moles) which was collected was always pure EtOAc, as demonstrated by a comparison of the i.r. and ^1H n.m.r. spectra of this liquid with those of an authentic sample of EtOAc.

$$MgCl_2 \cdot TiCl_4 \cdot 4EtOAc \xrightarrow{80^\circ C} MgCl_2 \cdot TiCl_4 \cdot 2EtOAc + 2EtOAc$$

At higher temperatures (120°C) the yellow solid charred to a black powder.

The complex (I) was found to dissolve in chloroform to give approximately 0.05M solutions, and it was also soluble in dichloromethane, but insoluble in benzene, toluene and hexane. When a suspension of (I) with benzene was refluxed the clear solvent gradually

turned yellow, though the solid did not appear to dissolve. When the residue was isolated by syringing off the solvent, washing with petroleum ether, and drying in *vacuo* it was found to be the EtOAc adduct of $MgCl_2$, by comparison of its spectra with those of an authentic sample. The complex $(TiCl_4 \cdot EtOAc)_2$ crystallized from the benzene solution. Therefore under these conditions (I) decomposes according to the equation:

$$2MgCl_2 \cdot TiCl_4 \cdot 4EtOAc \rightarrow (TiCl_4 \cdot EtOAc)_2 + 2MgCl_2 \cdot xEtOAc + EtOAc$$

2.6.2. Spectroscopic Properties of $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$

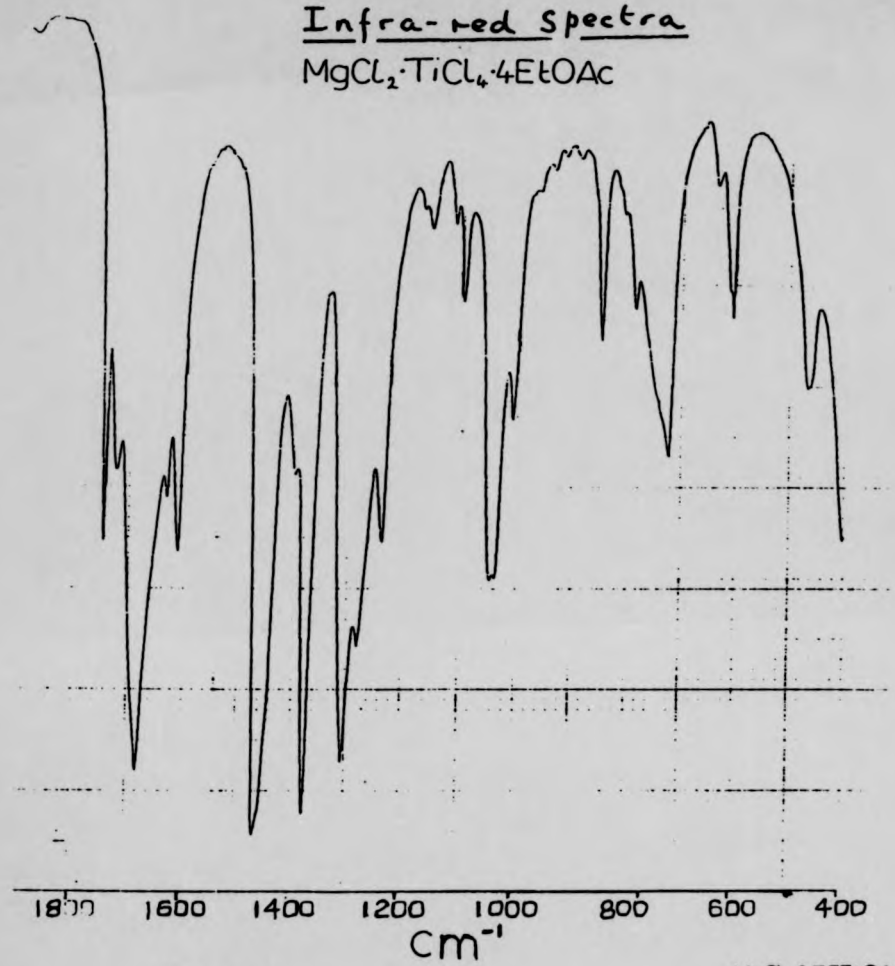
The i.r. spectrum of (I) in the carbonyl stretching region was complicated. Bands were observed at 1720, 1680 and 1615 cm^{-1}, and if the solid was not thoroughly pumped a band at 1743 cm^{-1} was observed, which corresponds to unco-ordinated EtOAc.

A very weak band at 1720 cm^{-1} which was often observed, arises from traces of water co-ordinated to magnesium in the anhydrous $MgCl_2$ used as starting material, as mentioned above.

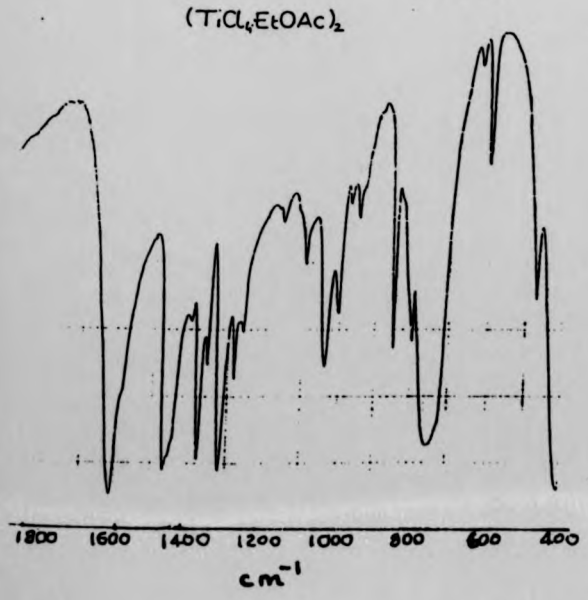
The major band in the i.r. spectrum in the carbonyl region was at 1680 cm^{-1}. This is consistent with co-ordination of the ester to magnesium by the

Infra-red Spectra

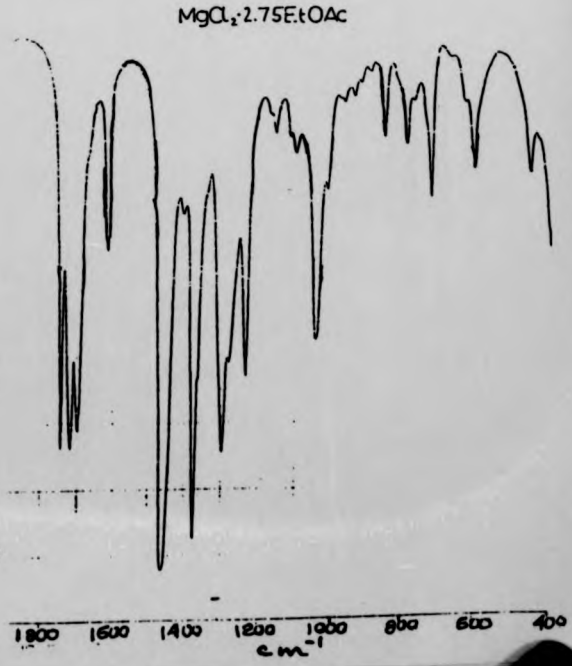
$MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$



$(TiCl_4 EtOAc)_2$



$MgCl_2 \cdot 2.75 EtOAc$



carbonyl group, since the carbonyl stretching frequency of EtOAc co-ordinated to $MgCl_2$ was found to be at 1700 cm^{-1}, whereas in $(TiCl_4 \cdot EtOAc)_2$ it occurs at 1615 cm^{-1}.

Bands in the Ti-Cl stretching region of the i.r. spectrum of (I) were found at 390, 345 and 290 cm^{-1}. This indicates a bis-adduct of $TiCl_4$ which has *cis* geometry, where three bands would be expected. The bands associated with the stretches of the bridging chlorides are likely to be found at lower wavenumbers than were recorded.

The solution properties of complex (I) were investigated using ^1H n.m.r. spectroscopy. It is known that in the solid state it is the carbonyl oxygen of esters which acts as the donor atom, and the structure of (I) in the solid state (Section 2.4.5.) shows that the ester is co-ordinated to the magnesium centre. The present results indicate that a different situation may apply in solution as outlined below. Thus, using $CDCl_3$ solutions of comparable molarity, the chemical shifts of the protons in the ligand under different circumstances are shown below.

$$\underset{(C)}{CH_3} - \underset{(B)}{CH_2} - O \backslash \; / C = O \rightarrow M$$
$$CH_3 \; (A)$$

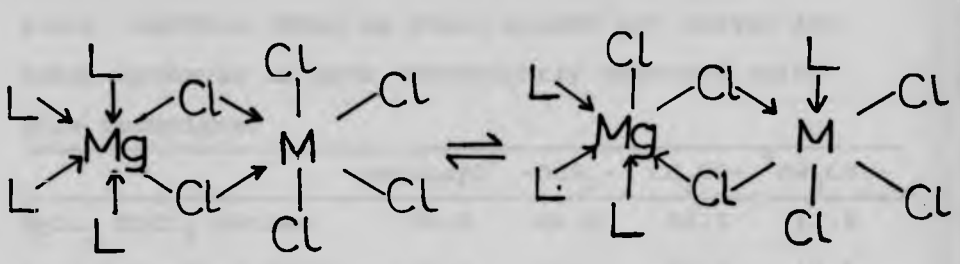
	Proton Shifts†		
	(A)	(B)	(C)
$CH_3COOCH_2CH_3$ (EtOAc)	2.05	4.13	1.26
$(TiCl_4 \cdot EtOAc)_2$	2.55	4.50	1.42
$MgCl_2 \cdot 2.75EtOAc$	2.08	4.13	1.26
$MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$	2.33	4.32	1.34

†Shifts are given in p.p.m. positive values representing downfield shifts from internal reference, TMS = 0.

The results clearly show that co-ordination of the ligand to the metal centre causes a downfield shift in all the proton resonances, with the effect being most marked in the case of the acyl protons (A), as might be expected. The very small shift (0.03 p.p.m.) observed for the magnesium compound alone is noteworthy, but recognising the instability and insolubility of this solvate the value is probably influenced by exchange between free (dissociated) and bound EtOAc.

The most interesting feature of the results is that the shifts of the ligand protons in (I) are very close to the average values of the shifts for $(TiCl_4 \cdot EtOAc)_2$ and $MgCl_2 \cdot 2.75$ EtOAc. While such a result could be fortuitous, two observations suggest an alternative explanation. Firstly, the ligands in (I) are labile as shown below, and secondly, dissociation of (I) into $(TiCl_4 \cdot EtOAc)_2$ and $MgCl_2 \cdot xEtOAc$

occurs under mild conditions as shown above. It is not unreasonable therefore to suggest that in solution a rapid exchange of ligands occurs between the magnesium and titanium centres via a partial chloro-bridge opening process:



However, it should also be pointed out that there is still no direct evidence for the existence of such an intramolecular process. Further evidence relevant to this discussion is presented in Sections 2.6.6. and 2.6.7.

If co-ordination was through the acyl oxygen the quartet which is due to the methylene (B) of the ethyl group would have been most affected.

The ligands in (I) were shown to be labile in $CDCl_3$ solution, because on addition of one mole equivalent of EtOAc to (I) only <u>one</u> set of resonances (corresponding to proton sets A, B and C) is observed in the ^1H n.m.r. spectrum, at room temperature, which were intermediate between those of free EtOAc and (I).

The resonances were observed to move upfield as successive molar amounts of free EtOAc were added. The relatively small shifts observed in the ^{1}H n.m.r. spectra make it difficult to follow this exchange using this technique, but the shifts observed in ^{13}C n.m.r. spectra (data as shown below) are larger and hence exchange is more conveniently observed using this technique.

	carbonyl[†]	$-OCH_2-$	$^{*}CH_3CO-$	$^{*}CH_3CH_2-$
$MgCl_2$ $TiCL_4$ 4EtOAc	178.2	64.8	22.7	14.9
+ 1 mole free EtOAc	176.3	63.7	22.4	14.9
2 " " "	175.9	63.3	22.2	14.9
4 " " "	175.1	62.8	22.1	14.9
6 " " "	174.4	62.5	22.0	14.8
12 " " "	173.6	62.1	21.8	14.8
24 " " "	172.9	61.6	21.5	14.7
48 " " "	172.4	61.4	21.4	14.7
96 " " "	172.1	61.1	21.3	14.7
free EtOAc	170.7	60.4	20.8	14.4

[†]Shifts are given in p.p.m., with respect to an external reference, dioxan = 67.4

Hence the resonances do not approach those of free EtOAc until the ligand is present in more than one hundred times excess.

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4 " " "	175.1	62.8	22.1	14.9
6 " " "	174.4	62.5	22.0	14.8
12 " " "	173.6	62.1	21.8	14.8
24 " " "	172.9	61.6	21.5	14.7
48 " " "	172.4	61.4	21.4	14.7
96 " " "	172.1	61.1	21.3	14.7
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†Shifts are given in p.p.m., with respect to an external reference, dioxan = 67.4

Hence the resonances do not approach those of free EtOAc until the ligand is present in more than one hundred times excess.

The variable temperature ^1H n.m.r. spectra of (I) are complicated, and will be discussed in detail in Section 2.6.6.

2.6.3. Displacement Reactions of $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$

In view of the lability of the EtOAc ligand reported above, it might be anticipated that complex (I) could provide a suitable starting material for the preparation of a series of related complexes by ligand displacement reactions. Such reactions, if successful, would be particularly useful because they would offer a convenient preparation of a series of complexes related to (I). Otherwise such complexes probably would be difficult to prepare in that a solution of $MgCl_2$ in the appropriate ligand is required initially for a convenient preparation. There is also the possibility of preparing mixed ligand complexes (e.g. $MgCl_2 \cdot TiCl_4 \cdot 2L \cdot 2L'$) by partial displacement.

The reactivity of (I) towards other ligands was investigated by adding these ligands to solutions of (I) in $CDCl_3$ and following the reactions by ^1H n.m.r. spectroscopy. The observations are presented in the Table overleaf.

When strong donors such as DMSO or pyridine were added to solutions of (I) in $CDCl_3$ yellow precipitates formed immediately. The ^1H n.m.r. spectra of the

supernatants showed only free EtOAc; it appears therefore that strong donors completely disrupt the bimetallic complex, and the individual magnesium and titanium complexes (e.g. $TiCl_4 \cdot 2py$, etc.) precipitated from the solution.

When four mole equivalents of THF were added to a solution of (I) in $CDCl_3$ in a stepwise manner the ^1H n.m.r. resonances of EtOAc moved upfield until they corresponded exactly with those of free EtOAc when addition was complete. When this reaction was done on a preparative scale the solid isolated by the removal of solvent was identical to that produced by dissolving (I) in THF. The compound could be obtained more directly by mixing solutions of $TiCl_4$ and $MgCl_2$ in THF, and was identified by analysis as $MgCl_2 \cdot TiCl_4 \cdot 4THF$.

Integration of the ^1H n.m.r. resonances (values shown below) due to the carboxylate groups of the esters, EtOFm and EtOBz showed that these ligands displaced two of the four EtOAc ligands from (I), to produce complexes of the type $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc \cdot 2L$ in solution. These compounds could not be isolated as solids.

$MgCl_2 \cdot TiCl_4 \cdot 2EtOAc \cdot 2L$	$CH_3CO_2Et^\dagger$	$RCO_2Et^\dagger$
L = EtOFm	2.3 (6H)	8.3 (2H)
L = EtOBz	2.3 (6H)	7.5-8.5 (10H)

Values given in p.p.m. rel. to TMS=0, integrated intensities are given in brackets.

Displacement Reactions with $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$

Ligand	Conditions	Product	Remarks
THF	$CDCl_3$ solution in n.m.r. tube, and THF added	$MgCl_2 \cdot TiCl_4 \cdot 4THF$	Straightforward displacement takes place, where all EtOAc is replaced by THF
DMSO	$CDCl_3$ solution in n.m.r. tube, and DMSO added	Yellow precipitate	Stronger donor, probably breaks up bridges
Pyridine	Similar to above	Yellow precipitate	As above for DMSO
CH_3CN	Similar to above	Yellow precipitate	As above for DMSO
$P(OCH_3)_3$	Similar to above	Yellow solution several signals in n.m.r.	^1H n.m.r. shows 3 types of $P(OCH_3)_3$ present – indicates split up of complex with xs $P(OCH_3)_3$
EtOBz	Similar to above, and isolation of product on larger scale attempted	Displacement observed though not complete	The solid isolated after addition of xs EtOBz still had EtOAc present
EtOAc	$CDCl_3$ solution in n.m.r. tube,	Exchange observed	EtOAc exchanges fast on n.m.r. time scale, only one set of ligand signals

The compound formulated as $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc \cdot 2EtOFm$ was observed in solution when two or more moles of EtOFm were added to a solution of (I) in $CDCl_3$, and excess ligand was removed by pumping.

A similar procedure could not be followed with EtOBz, due to the involatility of this ester. However, whenever more than two mole equivalents of EtOBz were added to solutions of (I) free EtOBz was observed at 1700 cm^{-1} in the i.r. spectra of the solutions, and on pumping two mole equivalents of EtOAc were lost.

The reaction of $P(OMe)_3$ with (I) was complex. Initially straightforward displacement of EtOAc was observed, as the EtOAc signals in the ^1H n.m.r. spectrum moved closer to the values found in the free ligand, when up to three mole equivalents of $P(OMe)_3$ were added to a solution of (I) in $CDCl_3$. When four mole equivalents of $P(OMe)_3$ were added two new signals were observed at 4.0 and 3.7 p.p.m., which probably correspond to individual complexes of $P(OMe)_3$ with $TiCl_4$ and $MgCl_2$, which did not precipitate.

2.6.4. Preparation of Complexes Related to $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$

As described above it was not generally possible to prepare analogues of (I) by ligand displacement

reactions. Strong donors disrupted the system, while esters would not completely displace EtOAc, so the only ligand of those tested for which this was a successful method of preparation was THF.

The present results therefore indicate that the best general method for preparing complexes of type (I) remains that which uses a solution of $MgCl_2$ in the appropriate ligand as starting material. Such solutions are possible for THF,EtOFm, and the bi-functional ester diethyl succinate (DES), but not for example EtOBz.

Hence the compounds $MgCl_2 \cdot TiCl_4 \cdot 4L$ (L = EtOFm or THF) were prepared by similar procedures to that used in the preparation of (I).

Anhydrous $MgCl_2$ dissolved in both EtOFm and THF to give approximately 0.5M solutions. The bimetallic compounds were prepared by adding one mole equivalent of $TiCl_4$ to a cooled solution of $MgCl_2$ in the appropriate ligand, and heating for a few hours. In both cases the products were found to be very soluble in the parent ligand, and the yellow solutions had to be pumped almost to dryness before solids precipitated.

As in the preparation of (I) the supernatants were removed, and the solids were washed with petroleum ether, and then dried in *vacuo* for several hours. The THF complex was still not free flowing after this procedure so residual solvent had to be removed by

heating the solid to 60°C in *vacuo* for two hours.

The DES analogue of (I) was also prepared by adding (one mole equivalent) $TiCl_4$ dropwise to a solution of $MgCl_2$ in the ligand. Anhydrous $MgCl_2$ dissolved in dry DES to give an approximately 0.2M solution. The ligand DES was not volatile enough to be removed by pumping, but yellow crystals precipitated from solution on standing for a week at room temperature. These crystals were then isolated by removal of the solvent, washing with petroleum ether and drying in *vacuo*. However, the i.r. spectrum had a strong band at 1738 cm^{-1} which corresponds to unco-ordinated DES, as well as a band at 1690 cm^{-1} which is consistent with DES co-ordinated to magnesium. Further washing of the crystals with petroleum ether and benzene did not decrease the intensity of the band at 1738 cm^{-1} relative to that at 1690 cm^{-1}. Only one set of resonances were observed in the ^1H and ^{13}C n.m.r. spectra of the crystals in $CDCl_3$ solution, which were downfield of free DES.

The elemental analyses of the crystals correspond very closely to a formulation of $MgCl_2 \cdot TiCl_4 \cdot 3DES$, and it is therefore proposed that the compound is probably a direct analogue of (I) in that two DES molecules co-ordinate to magnesium as bidentate chelates, but one ligand molecule per molecule of

complex is unco-ordinated in the crystal lattice of the compound.

As only one set of resonances were observed in the ^{1}H and ^{13}C n.m.r. spectra of this compound in $CDCl_3$ solution this suggests that the free and co-ordinated ligands are in rapid exchange.

Attempts to prepare compounds with other potentially chelating esters, diethyl maleate (DEM), and di-isobutyl phthalate (DIBP), were unsuccessful. Magnesium chloride dissolved in DEM to give approximately 0.1M solutions, after the initial suspension had been heated to 100°C for 48 hours. If the solvent was refluxed the solid dissolved more rapidly, but discolouration of the solution took place, indicating some degradation of the ester. The precipitate which formed on standing, after one mole equivalent of $TiCl_4$ had been added to this solution in the normal way, was isolated by removal of the solvent, washing with petroleum ether and drying in *vacuo*. This solid was cream rather than yellow, and it consistently analysed as containing very little titanium relative to magnesium. It was therefore deduced that an analogue of (I) did not form with DEM as the ligand.

Anhydrous $MgCl_2$ was found to be almost totally insoluble in DIBP, but it did dissolve to give an

approximately 0.01M solution in the presence of an equimolar amount of $TiCl_4$. No solid precipitated from this solution until a ten-fold excess of toluene was added, and then a yellow amorphous powder formed, which was isolated by removal of the solvent, washing with petroleum ether and drying in *vacuo*. The i.r. spectrum of this solid showed only a strong band at 1690 cm^{-1} which was indicative of ester co-ordination to magnesium. In particular there was no band at 1648 cm^{-1}, where the carbonyl stretching frequency in the complex $TiCl_4 \cdot$DIBP occurs, or at 1730 cm^{-1} corresponding to the free ester. Elemental analyses of this solid were not consistent with any stoicheiometric complex, although the presence of both magnesium and titanium in the solid was confirmed.

2.6.5. Preparation of Complexes Related to (I), with Metals other than Titanium

As discussed in Chapter 1, $SnCl_4$ has a similar co-ordination chemistry to $TiCl_4$. Therefore it was not surprising that a directly analogous compound to (I), namely $MgCl_2 \cdot SnCl_4 \cdot 4EtOAc$ (II), was formed when one mole equivalent of $SnCl_4$ was added dropwise to a solution of $MgCl_2$ in EtOAc. In this case a white solid precipitated as the $SnCl_4$ was added, but this dissolved when the magnetically stirred

solution was heated to 60°C. White crystals formed as the clear solution was allowed to cool to room temperature. These were isolated in a similar manner to that used for (I).

The i.r. spectrum of (II) had a band at 1685 cm^{-1}, which was very close to that assigned to the carbonyl stretching frequency of EtOAc in (I), and is consistent with EtOAc also being co-ordinated to magnesium in (II).

The solution properties of (II) were found to be similar to those of (I). The EtOAc ligands were shown to be labile by ^{1}H n.m.r. spectroscopy, in that only one set of signals were observed for EtOAc when one mole equivalent of the free ligand was added to a $CDCl_3$ solution of (II). Four mole equivalents of THF completely displaced all the EtOAc from (II).

In the ^{1}H n.m.r. spectrum of (II) the signal corresponding to the acyl methyl group of EtOAC was found at 2.25 p.p.m., whereas in (I) it was found at 2.33 p.p.m. This would suggest that $TiCl_4$ has a slightly greater inductive effect on the $(EtOAc)_4MgCl_2$ unit than $SnCl_4$. This may indicate that the Mg:Ti linkage is stronger than the Mg:Sn linkage, although in view of the small difference involved such conclusions can only be regarded as tentative.

When equimolar amounts of $TiCl_4$ and $SnCl_4$ were both added to a $MgCl_2$ solution in EtOAc [ratio Mg:M=

1:1 (M = Ti, Sn)] the yellow crystals which formed on standing were isolated in the usual way. Elemental analyses of the crystals revealed the formulation $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12EtOAc$, and not $(MgCl_2)_8 \cdot (TiCl_4)_2 \cdot (SnCl_4)_3 \cdot 28EtOAc$ as previously reported [121].

The crystals proved interesting in that inspection using a microscope showed that there was only one type of crystal present, and that the solid was not therefore a mixture of individual crystals of (I) and (II) which had co-precipiated. X-ray analysis of the crystals revealed that they were isomorphous with (I), and had very similar unit cell dimensions. It would appear therefore that (I) and (II) were randomly arranged in the lattice, and that there was no order in the stacking of the different molecules (I) and (II). Several different samples were obtained from different solutions and analysed. The results showed that, within experimental error of the analytical figures, there was no variation in composition from one sample to another. It remains a matter for discussion as to whether the replacement of titanium by tin in (I) is completely random, in which case some variation in composition might be predicted, or whether a similar phase, having an essentially constant Ti:Sn ratio is always precipitated from solution.

Further, the mixture precipitated with the proportions of (I) and (II) in the same ratio regardless of the ratio of (I) and (II) in the reaction mixtures. Preparations in which the ratios of (I) and (II) varied between 1:5 and 5:1 were carried out, and in each case the product analysed close to $(MgCl_2)_3.TiCl_4.(SnCl_4)_2.12EtOAc$, although only small amounts of the product precipitated when the extreme ratios were used in the preparation.

The two components of the mixture could not be distinguished in the spectra of the crystals. Only one carbonyl stretching frequency, at 1685 cm^{-1}, was observed in the i.r. spectrum of the solid, and only one set of resonances were observed in the ^1H n.m.r. spectrum in $CDCl_3$, indicating that exchange of esters between (I) and (II) must be rapid.

The reason the crystals always had the same formulation, within experimental error is not clear as a statistical average of the compounds in the reaction, weighted according to their relative solubilities, might have been expected.

Analogues of (I), where $TiCl_4$ was replaced by $ZrCl_4$ and $HfCl_4$, were prepared by a similar procedure to that used for (I). Addition of the appropriate solid halide to EtOAc yielded a clear solution after heating to reflux for a few minutes.

One mole equivalent of $MgCl_2$, in EtOAc solution, was then added, and the mixture heated to 60°C for 1 hour. On cooling to room temperature, and standing over-night, amorphous white powders precipitated. The hafnium compound was less soluble than its zirconium analogue. Both compounds could be recrystallized from a minimum volume of EtOAc, but a crystalline product was only formed with the hafnium compound under slow cooling.

The i.r. spectra of the compound, $MgCl_2 \cdot MCl_4 \cdot 4EtOAc$ (M = Zr, Hf) were similar in the carbonyl region. The major bands being at 1690 and 1685 cm^{-1} respectively [c.f. 1680 cm^{-1} for (I)], indicating ester co-ordination to magnesium, as found in (I). Both compounds were hydrolysed rapidly by air.

Their solution properties were found to be similar to those of (I), in that the ester ligands were labile, and could be fully displaced by four mole equivalents of THF. However, the ^1H n.m.r. spectra of these compounds are complicated by exchange processes, so these will be discussed in detail in Section 2.6.6.

It did not prove possible to prepare mixed complexes of the type $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12EtOAc$ with $ZrCl_4$. Thus when $ZrCl_4$ was dissolved in EtOAc, and an equimolar amount of $SnCl_4$ was added, followed by two mole equivalents of $MgCl_2$ in EtOAc solution,

and the resulting clear solution heated to 60°C for 4 hours, a white amorphous solid precipitated on cooling. This was isolated by removal of the solvent, washing with petroleum ether and drying in *vacuo*. Analysis of this solid showed that it had a variable composition close to $(MgCl_2)_2 \cdot (SnCl_4) \cdot (ZrCl_4) \cdot 8EtOAc$. Solids prepared using other starting ratios of the reactants also had variable compositions. These systems obviously behave differently from the titanium systems, and are more in accord with what might be expected for different mixtures. The reason for the unique behaviour of the titanium/tin system may possibly arise from the closeness in size of $TiCl_4$ and $SnCl_4$.

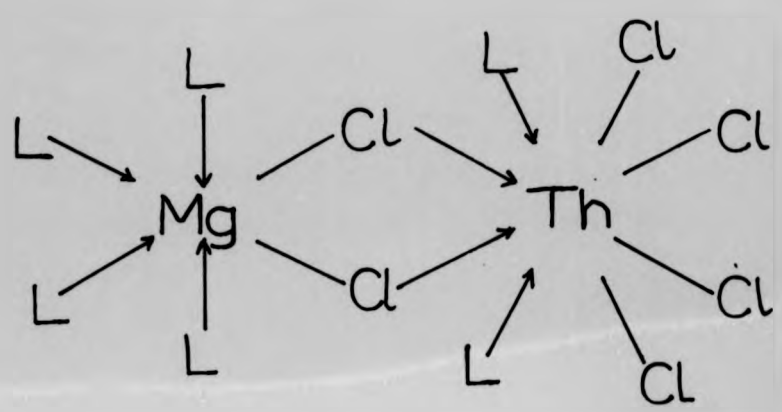
A further compound which was prepared for comparative purposes was that containing thorium tetrachloride. Addition of a solution of $ThCl_4$ in EtOAc to one molar equivalent of $MgCl_2$ in EtOAc immediately yielded a fine white precipitate. This dissolved to give a clear solution when heated to 60°C for 2 hours, and the white crystals which formed immediately on cooling to room temperature, after washing and drying in the usual way, analysed as $MgCl_2 \cdot ThCl_4 \cdot 6EtOAc$.

Thorium is the first member of the actinide elements, and shows some similarities to the Group IVA elements in its properties, especially in showing a predominant oxidation state of (IV). The co-

ordination chemistry of $ThCl_4$ is similar to that of $ZrCl_4$ and $HfCl_4$, though it has a greater tendency to form complexes with co-ordination numbers of greater than six[125].

The i.r. spectrum of $MgCl_2 \cdot ThCl_4 \cdot 6EtOAc$ in the carbonyl stretching region showed a strong band at 1685 cm^{-1} which had a shoulder at 1630 cm^{-1}. This suggests that in this case EtOAc is co-ordinated to both magnesium and thorium. The major carbonyl stretching bands in the spectra of (I) and (II) are found near 1685 cm^{-1}, while the major band in the spectrum of the solid isolated from a solution of $ThCl_4$ in EtOAc was at 1630 cm^{-1}. The EtOAc adduct of $ThCl_4$ was not fully characterised as it seemed to have a variable composition, which was dependent on the time of drying, but was approximately $ThCl_4 \cdot 2.5EtOAc$.

Therefore it is proposed that the usual $(EtOAc)_4 MgCl_2$ fragment bridges to $ThCl_4$, but that two molecules of EtOAc are also co-ordinated to the eight co-ordinate thorium atom.



The ^1H n.m.r. spectrum of this compound in $CDCl_3$ solution was consistent with this proposed structure. Only one set of signals were observed at room temperature, but these were further downfield than would be expected for EtOAc co-ordinated to magnesium, as the signal corresponding to the acyl methyl group was at 2.30 p.p.m. At -50°C the signals broadened, though they did not completely separate, indicating a rapid exchange of EtOAc between magnesium and thorium.

2.6.6. Variable Temperature ^1H n.m.r. Spectra of the Compounds $MgCl_2 \cdot MCl_4 \cdot 4EtOAc$ (M = Ti, Zr, Hf)

(i) $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$

The resonances in the spectra of (I) were sharp until the temperature was -84°C. At this temperature splitting of the singlet due to the acyl methyl was observed.

At a temperature of -90°C two singlets were clearly observed, and splitting of the quartet and triplet was apparent.

When the temperature was lowered further to -105°C, three separate singlets were resolved. Three quartets were also apparent but not fully resolved, while two of the expected three triplets were apparent but not well resolved.

The positions and relative intensities of the singlets observed in the spectrum recorded at -105°C are shown in the Table below.

δ (p.p.m.)	rel.int.(%)
2.32	50
2.38	47
2.59	3

(ii) $MgCl_2 \cdot ZrCl_4 \cdot 4EtOAc$

In the spectrum of this compound at +60°C all the signals were sharp and the multiplets were well resolved.

At 22°C the multiplets were not resolved and the singlet was broad. At 10°C splitting of the singlet was observed, and at 0°C two singlets and two quartets were clearly resolved, though the triplets remained unresolved.

When the temperature was lowered further to -30°C, the singlet at lower field was observed to split further, and -40°C three separate singlets were clearly resolved (and the signal at lowest field appeared to be splitting further). Their positions and relative intensities are shown in the Table below.

δ (p.p.m.)	rel.int.(%)
2.32	85
2.59	9
2.64	6

(iii) $MgCl_2 \cdot HfCl_4 \cdot 4EtOAc$

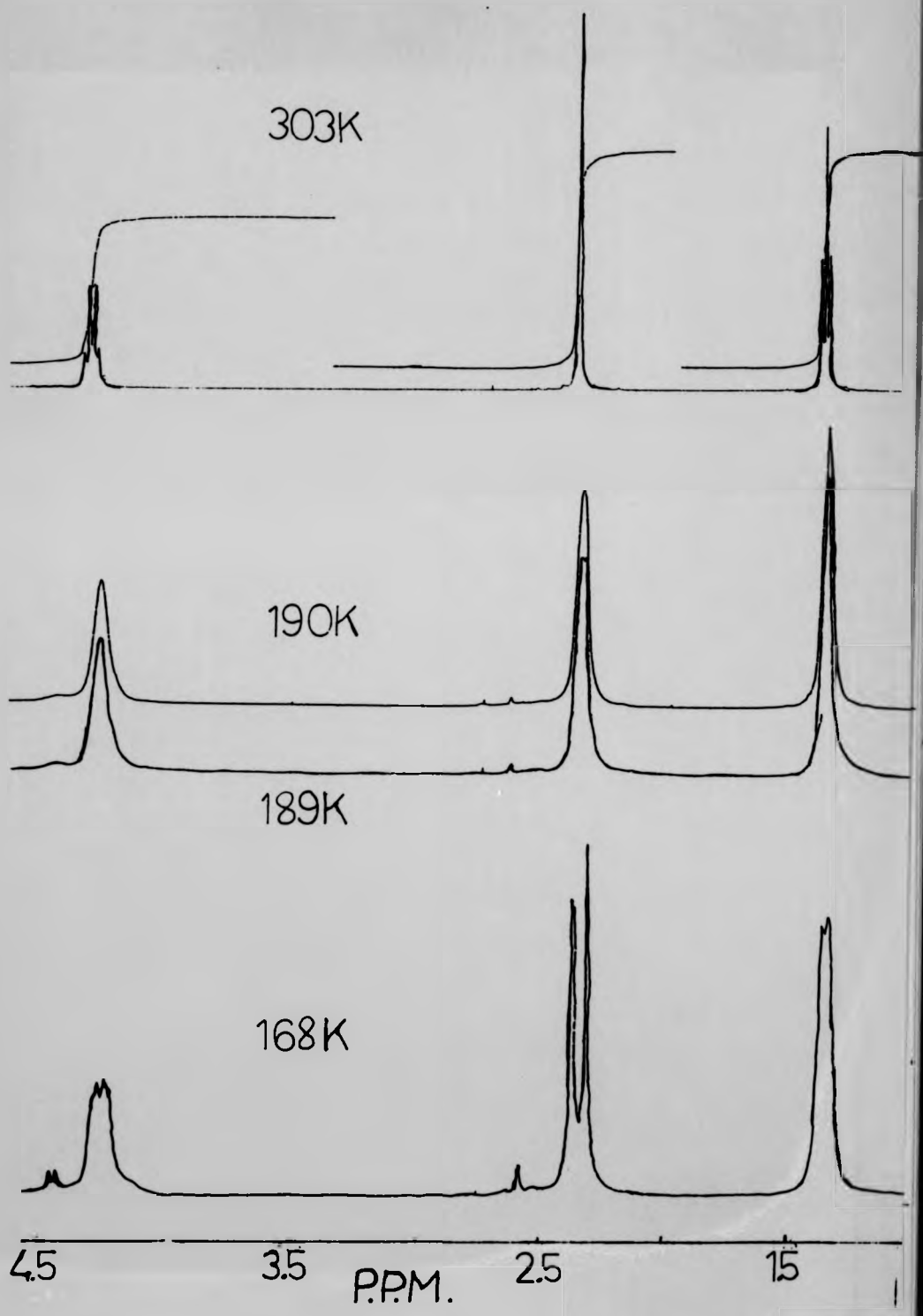
In this case even at + 60°C the signals in the spectrum of this compound were broad and the multiplets were unresolved. At + 50°C the singlet at 2.28 p.p.m. was observed to separate into two signals. When the temperature was lowered to + 40°C two singlets and two quartets were clearly resolved, and at + 20°C two triplets were apparent.

On further lowering of the temperature to - 30°C more splitting of the signals was apparent, and four separate sets of signals were resolved. Their positions and relative intensities are shown in the table below.

triplet (p.p.m.)	singlet (p.p.m.)	quartet (p.p.m.)	rel.int.(%)
1.21	2.25	4.23	71
1.39	2.56	4.55	11
1.43	2.60	4.57	13
1.50	2.70	4.73	5

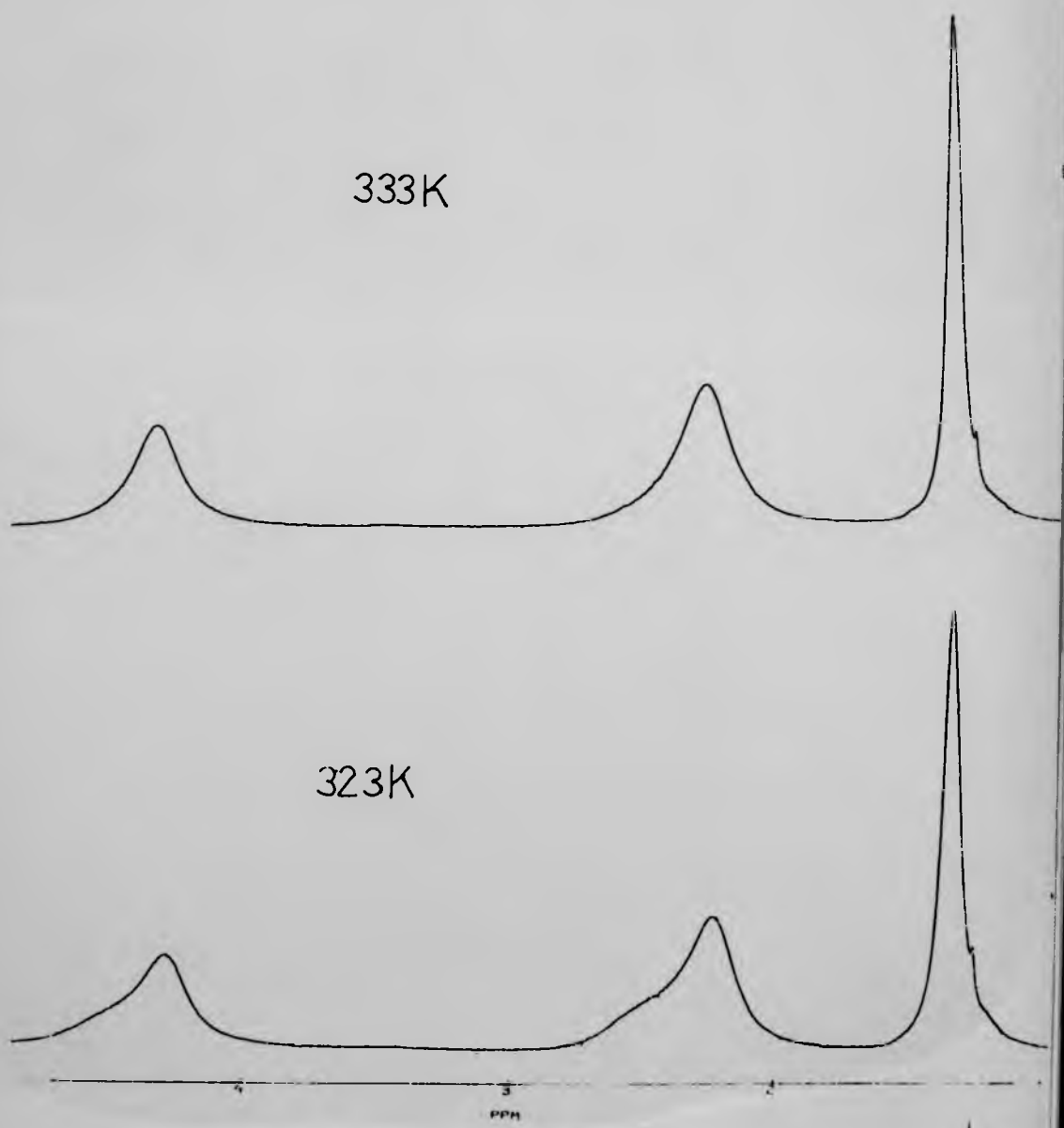
^{1}H n.m.r. spectra

$MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$

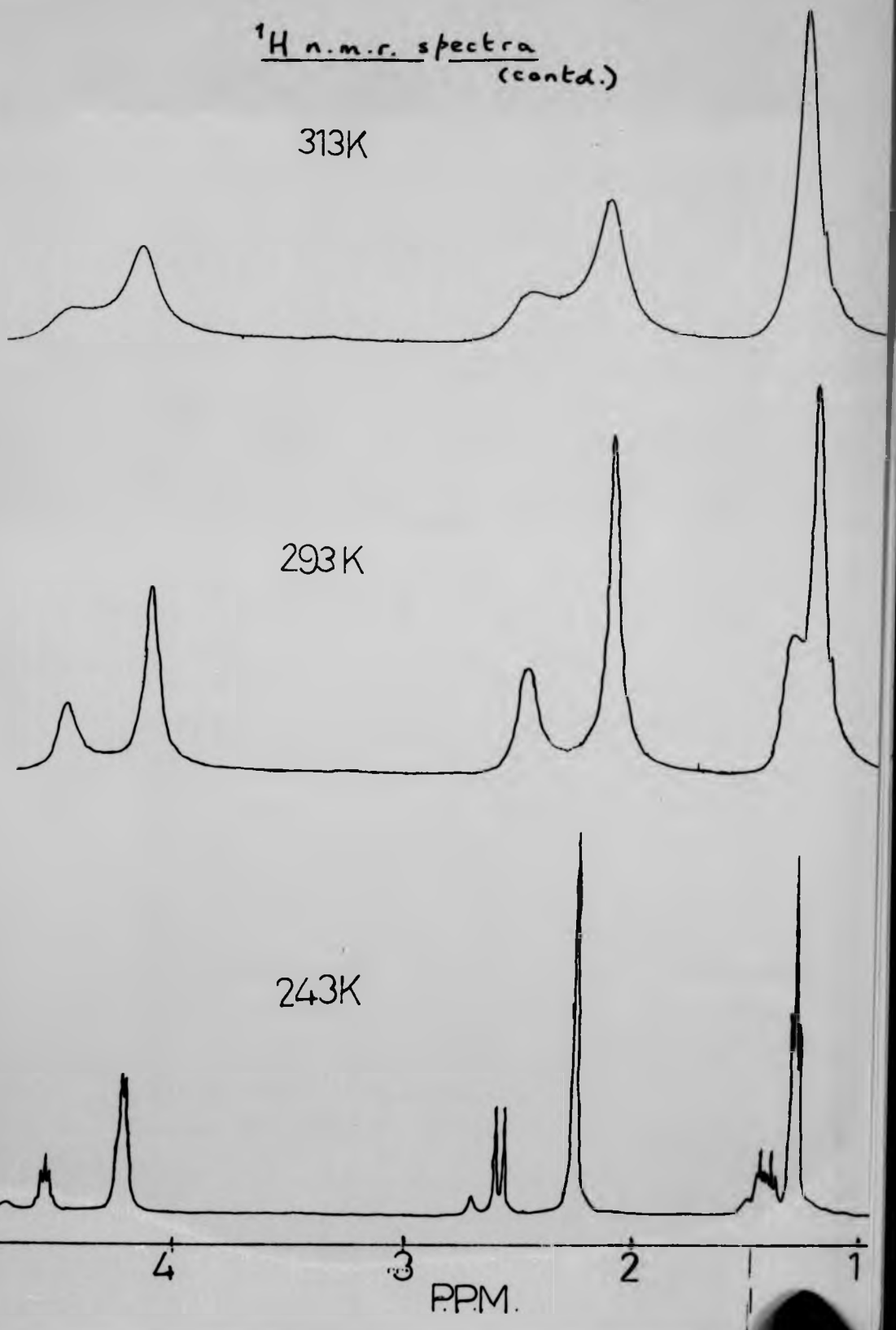


^{1}H n.m.r. spectra

$MgCl_2 \cdot HfCl_4 \cdot 4EtOAc$



^{1}H n.m.r. spectra (contd.)



2.6.7. Discussion of Spectra

These observations clearly indicate that exchange processes take place in the solutions of all these compounds. The processes decrease in rate as the Group IVA element becomes larger, as indicated by the approximate coalition temperatures measured from the ^{1}H n.m.r. spectra of these compounds for the major exchange process,

Ti, $-84^{o}C$; Zr, $10^{o}C$; Hf, $50^{o}C$.

The low temperature spectra of these systems showed that several species were present. As it was not possible to assign structures to these species a quantitative treatment of the equilibria was not attempted.

The spectra of the three compounds have features in common in that the set of resonances at highest field (triplets 1.3, singlets 2.3, quartets 4.25 p.p.m.) are all at similar chemical shifts, and all are the major species present (~ 80%). These signals are assigned to EtOAc co-ordinated to magnesium. They are all downfield of unco-ordinated EtOAc (t, 1.26; s, 2.05; q, 4.13), and as all the EtOAc is co-ordinated to magnesium in the solid phase it is reasonable that in solution the majority of it remains bound in the same way.

All the other sets of signals are further downfield

(triplets 1.4 - 1.5; singlets 2.5 - 2.7, quartets 4.5 - 4.7), and are at chemical shifts close to those expected for EtOAc co-ordinated to a Group IVA element [e.g. $(TiCl_4 \cdot EtOAc)_2$ t, 1.42; s, 2.55; q, 4.50 p.p.m.]. Therefore these signals can reasonably be assigned to EtOAc co-ordinated to a Group IVA element rather than magnesium.

There are differences between the titanium system, and the zirconium and hafnium. Only three sets of signals are observed in the lowest temperature spectrum of (I) ($-105^{\circ}C$), as opposed to four in those of the zirconium and hafnium analogues. This may be due to the relative rates of the exchange processes on these metals, and more species might be observed in the spectrum of (I) if it was possible to lower the temperature further.

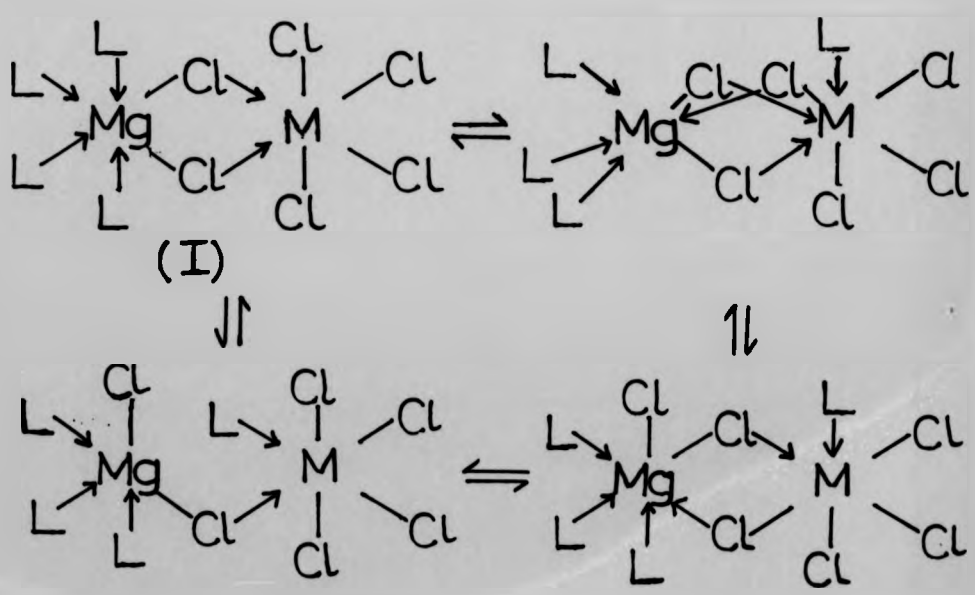
Perhaps more significantly the intensities of the signals assigned to EtOAc co-ordinated to zirconium or hafnium were all low compared to the major resonance in the spectra of $MgCl_2 \cdot MCl_4 \cdot 4EtOAc$ (M = Zr, Hf). In contrast in the spectrum of (I) two sets of signals were observed which are close in chemical shift, and of nearly equal intensity.

It was not possible to assign all the resonances observed in these spectra unambiguously, but it is possible to envisage several processes by which EtOAc could become co-ordinated to the Group IVA element.

If exchange between the ligands on magnesium was slowed then separate signals might be observed for equatorial and axial EtOAc molecules co-ordinated to magnesium. The signals of similar chemical shift and intensity of the spectrum of (I) are consistent with this proposal. Ligands could become co-ordinated to the transition metal if the dimeric complexes decomposed in solution thus

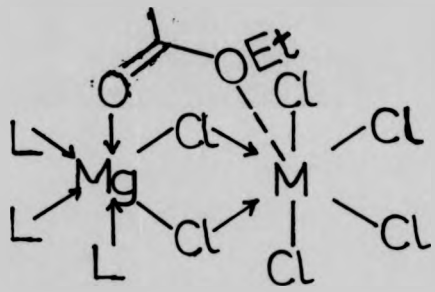
$$MgCl_2 \cdot MCl_4 \cdot 4EtOAc \rightleftarrows MgCl_2 \cdot 2EtOAc + MCl_4 \cdot 2EtOAc$$

Alternatively a ligand could become co-ordinated to the transition metal if the dimer remained intact if a process similar to that shown below was possible in solution. This is especially relevant to the properties of (I) itself discussed in Section 2.6.2.



A seven co-ordinate intermediate such as that shown above is not unreasonable, especially for zirconium and hafnium.

A further possibility, although probably less likely than those above is that if an EtOAc molecule bridged both the magnesium and the transition metal atoms, this would also produce signals at low field in the ^{1}H n.m.r. spectra of these solutions.



The assumption is made that the resonances observed for EtOAc co-ordinate to magnesium in these different species are very similar and thus contribute to the signals found at highest field in all the spectra.

Hence these observations are consistent with the species identified in the solid state being the major species present in solution but other minor species are also observed. Some of the ligand is likely to be co-ordinated to the transition metal in these species. Only very tentative proposals

would be made for the structures of such species, but it is interesting to note the successive decrease in the rate of exchange down the series Ti > Zr > Hf. Unfortunately so far as we are aware there are no other results available where a direct comparison of exchange rates at zirconium and hafnium centres have been made, although the present results indicate that such a comparison may well lead to significant differences.

2.6.8. Further Reactions of $MgCl_2$ in EtOAc Solution

Attempts to prepare compounds in which $MgCl_2$ bridged to species other than metal tetrahalides were not successful.

When a solution of $MgCl_2$ in EtOAc was added to EtOAc solution of equimolar amounts of $CpTiCl_3$, $(PhO)_2TiCl_2$, $MeSnCl_3$, and Me_2SnCl_2, solids precipitated from the reaction mixture in each case, which were washed and dried in the usual way. The i.r. spectra of the solid precipitates in the carbonyl stretching region were identical to that of the $MgCl_2$/EtOAc solvate, indicating that complexes did not form.

Only trace amounts of EtOAc were observed in the ^1H n.m.r. spectra of solutions of these compounds in $CDCl_3$. This was consistent with EtOAc co-ordinated to $MgCl_2$ in forming the relatively insoluble

$MgCl_2$/EtOAc solvate, but not co-ordinating to the other species present.

It was concluded that the $(EtOAc)_4MgCl_2$ unit was not a strong enough donor to bond to these compounds, which were all weaker Lewis acids than the tetrachlorides.

2.6.9. Reactions of $MgCl_2$ with $TiCl_3$ and VCl_3 in EtOAc

The results of the reactions of $MgCl_2$ with titanium and vanadium trichlorides were somewhat inconclusive.

Solid VCl_3 was dissolved in EtOAc using a Soxhlet apparatus to give a standard solution, an equimolar amount of $MgCl_2$ in EtOAc was added, and the resulting mixture was heated to 60°C for 4 hours. No solid precipitated from this purple solution until most of the solvent had been removed by pumping, when a brown solid resulted. This solid had a variable composition, but was near $(MgCl_2)_2 \cdot (VCl_3)_3 \cdot 6EtOAc$, and therefore was not regarded as a discrete compound.

A similar procedure was followed with $TiCl_3$, in that a green solution of $TiCl_3$ in EtOAc was mixed with an equimolar amount of $MgCl_2$ in EtOAc. In this case green platelets precipitated when the resulting solution was allowed to stand for several weeks. This solid was isolated in the usual way and when fresh

analysed as $MgCl_2 \cdot TiCl_3 \cdot 3EtOAc$. The i.r. spectrum of this solid showed two bands in the carbonyl stretching region, at 1680 and 1640 cm^{-1}. This is consistent with EtOAc co-ordinated to magnesium and Ti(III), as the major bands in the carbonyl stretching region of (I) was found at 1685 cm^{-1}, and that of $TiCl_3 \cdot 3EtOAc$ was found in this work to be at 1640 cm^{-1}. This adduct was prepared as a comparison for the $MgCl_2$-containing solid, and is discussed below.

On standing over a month $MgCl_2 \cdot TiCl_3 \cdot 3EtOAc$ lost EtOAc, and then analysed close to $MgCl_2 \cdot TiCl_3 \cdot 2EtOAc$. It is not clear if the original green solid is an unstable compound, or is a mixture of the two unstable solvates $MgCl_2 \cdot 2.75EtOAc$, and $TiCl_3 \cdot 3EtOAc$.

The EtOAc adduct of $TiCl_3$ was prepared by dissolving $TiCl_3$ in EtOAc using a Soxhlet apparatus. Concentration of the resulting green solution, and standing for a week resulted in the precipitation of green crystals of $TiCl_3 \cdot 3EtOAc$. These were isolated in the normal way, but were observed to decompose quickly under reduced pressure to a grey amorphous solid. At atmospheric pressure decomposition also took place so that after three days the composition of the grey solid produced was close to $TiCl_3 \cdot 1 \cdot 5EtOAc$. When this solid was heated to 100°C under reduced pressure (0.1 mm Hg) a yellow solid sublimed leaving an inhomogeneous black solid.

The yellow sublimate was determined to be $(TiCl_4 \cdot EtOAc)_2$ by comparison of its i.r. and ^1H n.m.r. spectra with those of an authentic sample. Therefore a disproportionation reaction had taken place, analogous to that of $TiCl_3 \cdot 3THF$, which was observed by Kern[53].

$$TiCl_3 \xrightarrow{EtOAc} TiCl_3 \cdot 3EtOAc \rightarrow TiCl_3 \cdot 1.5EtOAc \downarrow + (TiCl_4 \cdot EtOAc)_2 + "TiCl_2"$$

Analysis of the residue showed it to be low in titanium and chlorine content for $TiCl_2$, but its ability to reduce water indicated the presence of low valent titanium. Therefore it would appear that some decomposition of the ligand accompanies this reaction, and some organic material remains in the residue.

These observations indicated that a mixture of $MgCl_2$ and $TiCl_3$ adducts with EtOAc would probably be unstable with respect to loss of ligand, but a complex in which $MgCl_2$ bridged to $TiCl_3$ might also be unstable in this respect. Evidence in favour of the formation of bridged complex was that, when the solid containing $MgCl_2$ and $TiCl_3$ was heated, a disproportionation reaction was not observed, as it was with the pure $TiCl_3$ adduct of EtOAc.

2.6.10. Preparation of Complexes Related to (I) Containing Ethyl Benzoate

As noted earlier there is considerable interest in the complexes of aromatic esters with $MgCl_2$ and $TiCl_4$ because of their application in the preparation of propylene polymerization catalysts. As previously described in Section 2.6.3., it was not possible to prepare analogues of (I) by displacement of EtOAc by EtOBz in $CDCl_3$ solution. A second approach to the preparation of this type of compound was to attempt the displacement at higher temperatures in refluxing toluene, and then to distill the displaced EtOAc off at atmospheric pressure. Using this method any free EtOAc (b.p. 77°C) should be distilled out of the reaction mixture before the toluene (b.p. 110°C), but EtOBz (b.p. 180°C) should remain behind. Any equilibrium which exists between EtOAc and EtOBz should be moved towards co-ordination of EtOBz as EtOAc is removed.

Unfortunately this method did not succeed with (I), because at the elevated temperatures used the titanium complex charred, and a viscous black oil resulted. The tin analogue was less sensitive; this survived the toluene distillation temperature, and complete displacement of EtOAc was eventually achieved. Thus, when four mole equivalents of

EtOBz were mixed with a suspension of (II) in toluene, and the solvent distilled off, the residue after washing with petroleum ether and drying in *vacuo* was a colourless solid. The i.r. and ^1H n.m.r. spectra of the solid indicated that EtOAc was still present. Two separate sets of ester resonances were observed in the ^1H n.m.r. spectrum in $CDCl_3$ solution corresponding to EtOAc and EtOBz, and a band at 1743 cm^{-1} in the i.r. spectrum of the solid indicated surprisingly that free EtOAc was present, while bands at 1685 and 1660 cm^{-1} were consistent with two types of carbonyl groups co-ordinated to magnesium.

When this process was repeated a further five times the resulting white solid only contained a trace (~ 2%) of EtOAc, as indicated by the integral of the ^1H n.m.r. spectrum, and only the band at 1660 cm^{-1} remained in the i.r. spectrum of the solid. The product then analysed as $MgCl_2 \cdot SnCl_4 \cdot 4EtOBz$.

2.7. Polymerization Tests

The compounds $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$, $MgCl_2 \cdot ZrCl_4 \cdot 4EtOAc$, and $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_3 \cdot 12EtOAc$, were tested as polymerization catalysts for ethylene and propylene. The procedures followed

were identical so only the reaction of $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$ with ethylene will be described in detail.

Complex (I) (0.34 g, 0.5 mmol) was magnetically stirred in heptane (25 cm^3). A portion of the slurry (5 cm^3, 0.1 mmol) was transferred to the polymerization reaction vessel by syringe, and the total volume of heptane was made up to 500 cm^3. The solvent was degassed by purging with nitrogen, and $AlEt_3$ in heptane solution (10 cm^3, 1.0 mol dm^{-3}, 0.1 mmol) was added. Ethylene gas was then introduced to the reaction vessel which was kept at a constant pressure of one atmosphere as the reaction mixture was vigorously agitated.

The reaction was followed by measurements of the rate and volume of gas taken up. The solution became cloudy as white polymer was produced, and the supernatant slowly turned brown. The activity of the catalyst reached a maximum after 75 minutes, and then gradually lost activity over the period of the test which was a further 3 hours. The polymer was not isolated.

The results of the three tests are presented in the Table below.

	m.a.p.e.	t	profile	m.a.p.p.
(i)	340	75	rapid increase in rate until 75 min, then steady full off	20
(ii)	560	140	gradual increase in activity until 140 min. then near constant activity for 2 hours	30
(iii)	30		activity decreases constantly from the initial level	-

Key

m.a.p.e. is maximum activity for polyethylene polymerization, units are g of polymer produced per mmol of active metal per atmosphere of monomer.

m.a.p.p. is maximum activity for polypropylene polymerization, units as above.

t (min.) is the time taken to reach the maximum activity.

profile is a description of the activity change with time.

The results showed that $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$ and $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12EtOAc$ were both very active ethylene polymerization catalysts, and quite active propylene polymerization catalysts. The activity of the mixed complex was such that it could be a viable commercial catalyst. Its enhanced activity over (I) was thought to be due to "fragmentation". Catalysts with a very high titanium content are often less active than expected because polymer is made very quickly, and it rapidly becomes difficult for monomer

to reach the active centres. In systems such as $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12EtOAc$ the active sites are probably relatively far apart, so access to active centres is not as hindered, and also polymer when formed can break free from the catalyst and allow the catalytic centres to remain active.

The zirconium complex was only weakly active as in ethylene polymerization catalyst, and it was inactive as a propylene catalyst.

2.8. Summary

These studies have determined that the model found for (I) could be extended to the other Group IVA elements, and also to tin tetrachloride in the compound (II). An interesting mixed complex containing (I) and (II) was identified, though its structure has not been resolved. With slight modification the model held for thorium tetrachloride.

The ester ligands in the complexes $MgCl_2 \cdot MCl_4 \cdot 4EtOAc$ (M = Ti, Zr, Hf) were shown to be labile by exchange experiments, observed by ^1H n.m.r. spectroscopy. Low temperature spectra revealed that several species were present in solutions of these compounds.

It was found that EtOAc could be replaced in complexes of type (I) by other ligands in which $MgCl_2$ is soluble, such as EtOFm, DES, and THF.

However, in general compounds could not be prepared by complete displacement of EtOAc from (I); the THF adduct being the only exception. Displacement of EtOAc from (I) by other esters produced the complexes $MgCl_2 \cdot TiCl_4 \cdot 2EtOAc \cdot 2L$ in solution.

Investigations of (I) showed it to be a fragile compound. It decomposed in the presence of air or water, and was degraded by heat, either in solution or the solid phase. Strong donor solvents such as DMSO, and pyridine, disrupted (I), so clearly the chloro-bridge between magnesium and titanium was not strong enough to stay intact under any but the mildest conditions.

It was not possible to extend the model to other tetravalent titanium compounds, or to any trivalent compounds.

2.9. Experimental

All the compounds studied in this chapter of the thesis were air and moisture sensitive, and thus had to be handled in a nitrogen atmosphere using conventional Schlenk apparatus. Also all reagents and solvents had to be dried rigorously before use. The techniques, apparatus, and drying procedures used will be discussed in detail later.

2.9.1. Preparation of ester adducts of $TiCl_4$

Several ester adducts of $TiCl_4$ were prepared in the course of this work, in order to compare their spectral properties with those of the $MgCl_2$-containing compounds.

Preparation of $(TiCl_4 \cdot EtOAc)_2$

The adduct $(TiCl_4 \cdot EtOAc)_2$ was prepared as previously reported[29]. A solution of the adduct was prepared by adding $TiCl_4$ (2.0 cm^3, 18.3 mmol) dropwise, from a syringe to magnetically stirred EtOAc (10 cm^3) in a Schlenk tube at -30°C. Solvent was removed from the resulting yellow solution by pumping until a viscous oil remained. This was heated to 80°C under reduced pressure (0.1 mmHg), and yellow crystals of $(TiCl_4 \cdot EtOAc)_2$ sublimed and collected on the cooler parts of the Schlenk tube. These were washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours.

i.r.	1615(s)	1470(s)	1380(s)	1325(s)	1220(m)
	1160(w)	1095(w)	1040(s)	1005(m)	975(w)
	850(s)	720(m)	600(w)	470(m)	380(s)
	265(w) cm^{-1}				
^1H n.m.r.	1.42(t) (3H)	2.55(s) (3H)	4.50(q) (2H) p.p.m.		

Preparation of other ester adducts

The preparations of the other ester adducts were essentially identical. Synthesis of the EtOFm adduct was typical and will be described in detail, while any differences in the other preparations will be highlighted.

Preparation of $TiCl_4$·EtOFm

A solution of $TiCl_4$ (2.0 cm^3, 18.2 mmol) in petroleum ether (50 cm^3) was prepared by adding the $TiCl_4$ from a syringe dropwise to the solvent at 0°C. One mole equivalent of EtOFm (1.47 cm^3, 18.3 mmol) was added dropwise to this solution while it was magnetically stirred, and a yellow precipitate formed immediately. The supernatant was removed using a syringe and the solid washed with further petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. The product was a yellow powder (yield 4.7 g, 98%), which could be recrystallized from benzene solution.

i.r.	1625(s)	1545(mm)	1470(s)	1325(s)	1280(m)
	1300(m)	1270(m)	1155(s)	2005(m)	975(w)
	990(s)	850(s)	645(s)	470(m)	380(s) cm^{-1}

^1H n.m.r. 1.48(t) (3H) 4.59(q) (2H) 8.60(s) (1H) p.p.m.

Analysis based on $TiCl_4C_3H_6O_2$:

calculated:	Ti, 18.16;	C, 13.65;	H, 5.05%
found:	17.91	13.45	5.20

Preparation of $TiCl_4 \cdot EtOBz$

This was prepared by the procedure described above, though the product dissolved to give a yellow solution when heated in petroleum ether (b.p. 180°C), and formed large yellow crystals in essentially quantitative yield on cooling.

i.r.	1670(s)	1540(w)	1470(s)	1400(w)	1380(s)
	1300(s)	1155(w)	1115(w)	1100(m)	1040(s)
	1010(s)	850(m)	720(w)	635(w)	605(w)
	460(m)	350(s)	290(s)	215(m)	cm^{-1}

^1H n.m.r. 1.50(t) (3H) 4.72(q) (2H) 7.50-8.22(m) (5H)p.p.m

Analysis based on $TiCl_4C_9H_{10}O_2$:

calculated:	Ti, 15.52;	C, 32.73;	H, 3.03%
found:	14.50	32.90	3.05

Bifunctional esters

The adducts of the bifunctional esters, DES, DEM and DIBP were also prepared by the method of addition of the ester to a solution of $TiCl_4$ in petroleum ether. All three adducts were formed in quantitative yields, and could be recrystallized from toluene or benzene.

$TiCl_4 \cdot DES$

i.r.	1740(w)	1650(s)	1605(s)	1470(s)	1415(w)
	1380(s)	1355(w)	1300(m)	1255(s)	1230(w)
	1170(m)	1100(m)	1070(w)	1010(s)	980(w)
	910(w)	850(s)	780(m)	725(w)	400(m)
	370(s) cm^{-1}				

^1H n.m.r. 1.45(t) (6H) 3.05(s) (4H) 4.60(q) (4H) p.p.m.

Analysis based on $TiCl_4C_8H_{14}O_4$:

calculated:	Ti, 13.16;	C, 26.40;	H, 3.88%
found:	13.18	26.35	3.83

$TiCl_4 \cdot DEM$

i.r.	1738(w)	1665(s)	1630(s)	1470(s)	1435(m)
	1380(s)	1320(m)	1300(m)	1250(s)	1230(s)
	1170(w)	1100(m)	1010(w)	990(s)	935(w)
	880(w)	855(w)	830(s)	790(w)	725(w)
	430(w)	370(s) cm^{-1}			

^1H n.m.r. 1.48(t) (6H0 4.65(q) (4H) 6.72(s) (2H) p.p.m.

Analysis based on $TiCl_4C_8H_{12}O_4$:

calculated:	Ti, 13.24;	C, 26.55;	H, 3.34%
found:	13.20	26.60	3.39

$TiCl_4$·DIBP

i.r.	1730(w)	1680(s)	1615(m)	1580(m)	1495(w)
	1470(s)	1405(s)	1380(s)	1320(s)	1160(w)
	1125(w)	1090(m)	985(w)	970(w)	940(w)
	920(m)	900(w)	885(w)	800(w)	730(s)
	650(w)	600(w)	400(s)	380(s)	350(w)cm^{-1}

^1H n.m.r. 0.85(d) (12H) 2.28(m) (2H) 4.90(d) (4H)
7.5-7.8(m) (4H) p.p.m.

Analysis based on $TiCl_4C_{16}H_{22}O_4$:

calculated:	Ti, 10.23;	C, 41.06;	H, 4.74%
found:	10.16	41.32	4.68

The analyses of the ester adducts suggest that both the monodentate and bidentate esters formed 1:1 adducts. This suggests that the former were isomorphous with $(TiCl_4$·EtOAc$)_2$ and the latter are simple *cis* adducts in which the titanium atoms were six co-ordinate through bidentate co-ordination of the bifunctional esters. The infra-red spectra of the adducts were consistent with this, in that two bands are observed in the carbonyl stretching region which can be assigned to symmetrical and unsymmetrical stretching of the two co-ordinated carbonyl groups.

2.9.2. Preparation of $MgCl_2$ ester adducts

Preparation of $MgCl_2 \cdot 2.75EtOAc$

A standard solution of anhydrous $MgCl_2$ in EtOAc (0.40M) was prepared by adding EtOAc (500 cm^3) to solid anhydrous $MgCl_2$ (19.0g, 0.2M), and refluxing overnight. All the solid dissolved, but on standing for 14 days white needle-like crystals formed. Attempts to isolate these crystals appeared to yield different products depending on the time of pumping. The solid isolated by washing with petroleum ether (2 x 30 cm^3) and pumping for 5 minutes analysed as $MgCl_2 \cdot 2.75EtOAc$. As the time of pumping increased at a constant temperature of 25°C the constitution of the solid varied as follows: 5 min, 2.75 moles EtOAc; 0.5 hours, 1.96; 3 hours, 1.56; 18 hours, 0.94. When pumping took place at elevated temperatures then loss of ester was quicker, and a larger proportion of ester was lost. Pumping at 80°C for 8 hours resulted in a solid which had 0.56 moles of ester per mole of $MgCl_2$.

Thermogravimetric analysis of the solid indicated that there was a steady loss of ester up to 250°C, when only $MgCl_2$ remained.

$MgCl_2$/EtOFm

A standard (0.4M) solution of anhydrous $MgCl_2$ in

EtOFm was prepared exactly as for EtOAc. The solid adduct was similar to the EtOAc adduct in its stability but was not studied in the same detail.

$MgCl_2$/EtOBz

When anhydrous $MgCl_2$ (1.90g) was mixed with dry EtOBz (100 cm^3) and refluxed for 3 days none of the solid appeared to dissolve. The solvent was removed and the solid was washed with petroleum ether (2 x 50 cm^3) and dried in *vacuo* for 2 hours. The i.r. spectrum of the solid had no bands in the carbonyl stretching region, so it was deduced that $MgCl_2$ was unchanged by this treatment.

An alternative approach to the preparation of the EtOBz adduct of $MgCl_2$ was to add the EtOAc solvate of $MgCl_2$ (1.30g) to EtOBz (50 cm^3) and reflux the suspension for 5 hours. The EtOBz was then distilled from the suspension, which never dissolved. The white solid residue was washed with petroleum ether (2 x 50 cm^3) and then dried in *vacuo* for 4 hours. The i.r. spectrum of the solid (after treatment with EtOBz) was virtually identical to the spectrum before treatment, and no EtOBz was observed in the ^1H n.m.r. spectrum of a solution of the solid in $CDCl_3$. Therefore, even under these extreme conditions EtOBz did not displace EtOAc from $MgCl_2$.

$MgCl_2$/DES

A solution of anhydrous $MgCl_2$ in DES was prepared by adding DES (50 cm^3) to solid anhydrous $MgCl_2$ (0.91g) and heating to 100°C, with magnetic stirring for 3 hours. A clear solution resulted and a solid adduct was not isolated.

$MgCl_2$/DEM

A solution of anhydrous $MgCl_2$ in DEM was prepared by adding DEM (50 cm^3) to anhydrous $MgCl_2$ (0.63g) and heating to 100°C, with magnetic stirring for 48 hours. A clear solution resulted. However if the solution was heated to 150°C in order to accelerate the dissolution discolouration of the solution took place indicating that degradation of the ester took place.

$MgCl_2$/DIBP

When DIBP (50 cm^3) was added to anhydrous $MgCl_2$ (0.4g) and refluxed for 24 hours the solid did not dissolve to any observable extent. However the solubility of $MgCl_2$ in DIBP increased in the presence of $TiCl_4$ and this is described more fully in Section 2.9.3.

2.9.3. Preparation of complexes of the type $MgCl_2 \cdot MCl_4 \cdot 4EtOAc$

Preparation of $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$

$TiCl_4$ (2.0 cm^3, 18.2 mmol) was added dropwise,

from a syringe to a magnetically stirred solution of anhydrous $MgCl_2$ in EtOAc (45.8 cm^3, 0.4 mol dm^{-3}, 18.3 mmol) at 0°C. The resulting yellow solution was heated to 60°C and stirred for 4 hours. After cooling to room temperature the volume of the solution was reduced to approximately one-third of its original level by pumping, and a yellow solid precipitated. The supernatant was removed using a syringe, and the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. The solid could be recrystallized from a minimum volume of EtOAc to form small yellow crystals. The yield of the solid was dependent on the amount of solvent pumped from the solution because the product was very soluble in EtOAc, but when most of the solvent was removed the yield was essentially quantitative (10.0g, 90%).

The yellow solid was found to be soluble in $CHCl_3$, and CH_2Cl_2, but insoluble in benzene, toluene and petroleum ether.

i.r. 1743(w) 1720(w) 1680(s) 1615(w) 1460(s)
1380(s) 1300(s) 1280(m) 1235(m) 1155(m)
1115(w) 1095(w) 1045(s) 1005(m) 850(m)
720(m) 605(m) 460(m) 390(m) 345(s)
290(m) cm^{-1}

^1H n.m.r. 1.34(t)(3H) 2.33(s)(3H) 4.32(q)(2H) p.p.m.

^{13}C n.m.r. 14.9, 22.7, 64.8, 178.2 p.p.m.

Analysis based on $TiMgCl_6C_{16}H_{32}O_8$:

	Ti	Mg	C	H
calculated:	7.52;	Mg, 3.81;	C, 30.13;	H, 5.05.
found:	7.52	3.71	31.10	5.20

Preparation of $MgCl_2 \cdot TiCl_4 \cdot 4EtOFm$

The EtOFm complex was prepared by a similar procedure to that used in the preparation of (I) described above except that this compound proved very soluble in the ligand, and the volume of the solution had to be reduced almost to dryness before solid precipitated. (Yield 10.4g, 98%).

i.r. 1733(m) 1640(s) 1460(s) 1380(s) 1300(m)
1185(m) 1155(m) 1030(m) 930(w) 840(w)
720(s) 350(s) cm^{-1}

^1H n.m.r. 1.36(s)(3H) 4.38(q)(2H0 8.33(s)(1H) p.p.m.

Analysis based on $TiMgCl_6C_{12}H_{24}O_8$:

	Ti	C	H
calculated:	9.26;	27.87;	4.68%
found:	9.40	27,70	4.55

Preparation of $MgCl_2 \cdot TiCl_4 \cdot 4THF$

$TiCl_4$(2.0 cm^3, 18.3 mmol) was added dropwise to a solution of $MgCl_2$ in THF (36.6 cm^3, 0.50 mol dm^{-3}, 18.3 mmol) at 0°C. The resulting yellow solution was heated to 55°C, and magnetically stirred for 1 hour. The bulk of the solvent was removed by pumping at room temperature when a viscous oil resulted. This was heated to 60°C in *vacuo* for 4 hours, and a dry yellow powder was produced. This was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 1 hour. (Yield 10.5g, 98%)

i.r. 1460(s) 1380(s) 1300(w) 1170(w) 1070(w)
1020(s) 920(m) 870(s) 720(m) 675(m)
360(s) 345(s) 310(m) cm^{-1}

^1H n.m.r. 1.98(s)(4H) 3.75(s)(4H) p.p.m.

Analysis based on $TiMgCl_6C_{16}H_{32}O_4$:

	Ti	Mg	C	H
calculated:	8.92;	4.24;	33.50;	H,5.59%
found	8.96	4.10	34.22	6.03

Preparation of $MgCl_2 \cdot SnCl_4 \cdot 4EtOAc$

$SnCl_4$ (2.1 cm^3, 18.3 mmol) was added dropwise from a syringe to a solution of $MgCl_2$ in EtOAc (45.8 cm^3, 0.40 mol dm^{-3}, 18.3 mmol). White crystals formed immediately but all the solid dissolved when the solution was heated to 60°C and magnetically stirred for 4 hours. White crystals precipitated when the solution cooled to room temperature. The supernatant was removed, the crystals washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. (Yield 7.77g, 60%)

i.r. 1720(w) 1685(s) 1460(s) 1380(s) 1310(s)
1150(w) 1115(w) 1095(w) 1040(s) 1010(w)
850(m) 200(m) 640(w) 675(m) 460(m)
395(s) 315(s) 285(m) cm^{-1}

^1H n.m.r. 1.31(t)(3H) 2.25(s)(3H) 4.28(q)(2H) p.p.m.

Analysis based on $SnMgCl_6C_{16}H_{32}O_8$:

	Sn	Mg	C	H
calculated:	16.7;	3.44;	27.12;	H, 4.45%
found:	16.4	3.48	26.84	4.56

Preparation of $(MgCl_2)_3 \cdot TiCl_4 \cdot (SnCl_4)_2 \cdot 12EtOAc$

$TiCl_4$ (2.0 cm^3, 18.3 mmol) was added dropwise to a magnetically stirred solution of $MgCl_2$ in EtOAc (91.2 cm^3, 0.40 mol dm^{-3}, 36.6 mmol) at 0°C. $SnCl_4$ (2.1 cm^3, 18.3 mmol) was then added dropwise to the same solution, and the resulting yellow solution was heated to 60°C for 4 hours. After cooling to room temperature and standing for 16 hours yellow crystals formed in the solution. The supernatant was removed, the crystals washed with petroleum ether (2 x 50 cm^3), and dried in *vacuo* for 4 hours. (Yield 5.6g, 43%).

The ratio of $TiCl_4$:$SnCl_4$ was varied between 1:5 and 5:1 in the preparation but the same yellow crystals were formed in every case.

i.r. 1720(w) 1685(s) 1460(s) 1400(w) 1380(s)
1300(s) 1280(w) 1240(w) 1145(w) 1115(w)
1095(w) 1040(s) 1010(s) 850(s) 720(m)
650(w) 610(m) 460(m) 395(m) 350(m)
315(s) 290(m) cm^{-1}

^1H n.m.r. 1.31(t)(3H) 2.25(s)(3H) 4.28(q)(2H) p.p.m.

Analysis based on $TiSn_2Mg_3Cl_{18}C_{48}H_{96}O_{24}$:

calculated: Ti, 3.55; Sn, 11.5; Mg, 2.33; C, 28.05; H, 4.68%

found: 3.44 11.1 2.34 27.90 4.76

Preparation of $MgCl_2 \cdot ZrCl_4 \cdot 4EtOAc$

A solution of $ZrCl_4$ (2.6g, 11.2 mmol) in EtOAc (20 cm^3) was prepared adding the solvent to the solid

and heating to reflux for five minutes when a clear solution resulted. After the solution cooled to room temperature a solution of $MgCl_2$ in EtOAc (26.0 cm^{-3}, 0.40 mol dm^{-3}, 11.2 mmol) was added, and the resulting mixture was heated to 60°C and magnetically stirred for 1 hour. While still warm the solution was filtered through a celite pad, and white crystals formed on standing at -20°C overnight. The supernatant was removed, the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. (Yield 5.1g, 67%).

i.r.	1725(m)	1690(s)	1460(s)	1405(m)	1380(s)
	1305(s)	1280(m)	1235(m)	1160(w)	1115(w)
	1095(w)	1045(s)	1005(w)	850(m)	820(m)
	720(m)	635(m)	610(m)	470(m)	390(s)
	310(s)	290(s)	240(m) cm^{-1}		

^1H n.m.r. (room temp.) 1.34(t)(3H) 2.30(bs)(3H) 4.32(bs)(2H) ppm

Analysis based on $ZrMgCl_6C_{16}H_{32}O_8$:

calculated:	Mg, 3.57;	C, 28.20;	H, 4.74%
found:	3.64	27.85	4.78

Preparation of $MgCl_2 \cdot HfCl_4 \cdot 4EtOAc$

A solution of $HfCl_4$ (0.47g, 1.47 mmol) in EtOAc (30 cm^3) was prepared by adding the solvent to the white solid, and heating the mixture to reflux, when a clear solution resulted.

To this solution a solution of $MgCl_2$ in EtOAc ($3.67\ cm^3$, $0.40\ mol\ dm^{-3}$, 1.47 mmol) was added, and the resulting mixture was heated to 60^oC, with magnetic stirring for 1 hour. The solution was then filtered through a celite pad while still hot, and white crystals formed immediately on cooling. The supernatant was removed, the crystals washed with petroleum ether ($2 \times 30\ cm^3$), and dried in *vacuo* for 2 hours. (Yield 0.96g, 85%).

i.r. 1743(w) 1720(m) 1685(s) 1615(m) 1460(s)
1405(m) 1380(s) 1310(s) 1280(m) 1235(m)
1255(w) 1215(w) 1200(w) 1145(s) 1110(m)
850(m) 720(m) 640(m) 610(s) 645(s)
695(m) 230(s) cm^{-1}

^1H n.m.r. (room temp) 1.32(bs)(3H) 2.15(bs), 2.65(bs) (combined 3H) 4.20(bs), 4.60(bs) (combined 2H) p.p.m.

Analysis based on $HfMgCl_6C_{16}H_{32}O_8$:

	Mg,	C,	H,
calculated:	3.08;	25.00;	4.20%
found:	3.02	24.58	4.30

Preparation of $MgCl_2 \cdot ThCl_4 \cdot 6EtOAc$

A solution of $ThCl_4$ (0.90g, 2.40 mmol) in EtOAc ($50\ cm^3$) was prepared by adding the solvent to solid $ThCl_4$ and refluxing for 2 hours. A brown suspension resulted which was filtered through a celite pad to give a clear solution. A solution of $MgCl_2$ in EtOAc ($6.0\ cm^3$, $0.40\ mmol\ dm^{-3}$, 2.40 mmol) was added, and

the resulting solution was heated to 60°C and magnetically stirred for 2 hours. The solution was then filtered through a celite pad while still warm and white crystals formed as the solution cooled to room temperature. The supernatant was removed, the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. (Yield 0.62g, 30%).

i.r.	1743(w)	1715(m)	1680(s)	1640(m)	1620(w)
	1460(s)	1410(w)	1380(s)	1310(s)	1285(s)
	1235(m)	1160(w)	1120(w)	1095(m)	1045(s)
	1010(m)	850(m)	720(m)	640(m)	610(s)
	460(s)	400(s)	370(m)	300(m)	250(s)cm^{-1}

^1H n.m.r. 1.30(t)(3H) 2.30(s)(7H) 4.37(q)(2H) p.p.m.

Analysis based on $ThMgCl_6C_{24}H_{48}O_{12}$:

calculated:	Mg, 2.36;	C, 28.89;	H, 4.85%
found:	2.40	27.92	4.79

Preparation of $MgCl_3 \cdot SnCl_4 \cdot 4EtOBz$

EtOBz (1.38 cm^3, 9.60 mmol) was added to a suspension of $MgCl_2 \cdot SnCl_4 \cdot 4EtOAc$ (1.70g, 2.40 mmol) (ratio EtOBz:EtOAc=1:1) in toluene (50 cm^3). The suspension was refluxed for 30 minutes, and then the solvent was distilled from the solid. The solid was then washed with petroleum ether (2 x 50 cm^3), and dried in *vacuo* for 2 hours. This procedure was repeated a further four times until all the

EtOAc had been displaced.

i.r.	1730(w)	1700(w)	1660(s)	1600(m)	1585(m)
	1460(s)	1400(m)	1380(s)	1330(s)	1305(s)
	1275(s)	1180(w)	1160(w)	1150(w)	1110(m)
	1075(m)	1030(m)	1010(w)	1000(m)	950(w)
	860(m)	720(s)	690(m)	675(w)	530(m)
	395(w)	320(s)	285(s) cm^{-1}		

^1H n.m.r. 1.38(t)(3H) 4.50(q)(2H) 7.25-8.06(m)(5H)p.p.m.

Analysis based on $SnMgCl_6C_{36}H_{40}O_8$:

calculated:	Sn,12.5;	Mg, 2.48;	C, 45.75;	H, 4.27%
found:	12.6	2.56	45.30	4.25

Preparation of $MgCl_2 \cdot TiCl_4 \cdot 3DES$

$TiCl_4$ (1.15 cm^3, 9.56 mmol) was added dropwise to a solution of $MgCl_2$ in DES (50 cm^3, 0.19 mol dm^{-3}, 9.56 mmol) and heated to 80°C with magnetic stirring for 3 hours. On standing at room temperature for 3 days a few crystals formed, but on shaking the solution there was an immediate precipitation of a fine, microcrystalline yellow powder. The supernatant was removed, the solid washed with petroleum ether (2 x 50 cm^3), and benzene (3 x 50 cm^3), and dried in *vacuo* for 4 hours (Yield 5.51g, 80%).

i.r.	1740(s)	1690(s)	1470(s)	1422(w)	1380(s)
	1450(s)	1310(w)	1285(m)	1240(m)	1210(m)
	1170(s)	1120(w)	1095(m)	1070(w)	1030(s)
	965(w)	855(m)	800(m)	725(w)	645(w)
	570(w)	535(w)	460(w)	400(m)	350(s)
	300(m) cm^{-1}				

^1H n.m.r. 1.32(t)(6H) 2.80(s)(4H) 4.32(q)(4H) p.p.m.

Analysis based on $TiMgCl_6C_{24}H_{42}O_{12}$:

calculated:	Ti, 5.93;	Mg, 3.01;	C, 35.69,	H, 5.20%
found:	6.17	2.92	35.47	5.27

Reaction of $TiCl_4$ with $MgCl_2$ in DEM

$TiCl_4$ (2.95 cm^3, 26.9 mmol) was added dropwise to a solution of $MgCl_2$ in DEM (50 cm^3, 0.54 mol dm^{-3}, 26.9 mmol), and the resulting yellow solution was heated to 60°C and magnetically stirred for 4 hours. On standing at room temperature for five days a white, amorphous precipitate formed. The supernatant was removed, the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. The solid was not soluble in $CDCl_3$, gave a poorly resolved i.r. spectrum, and had a variable composition. Approximate analysis: Mg, 7.6; Ti, 4.5%.

Reaction of $TiCl_4$ with $MgCl_2$ in DIBP

A solution of $TiCl_4$ (3.56 cm^3, 32.5 mmol) in DIBP 950 cm^3) was added to anhydrous $MgCl_2$ (0.76g, 32.5 mmol), and the resulting suspension was heated to 100°C and magnetically stirred for 16 hours. The resulting yellow solution was filtered through a celite pad, and left to stand at room temperature. No precipitate was observed after 14 days so toluene

(250 cm^3) was added in five successive lots, and a yellow powder precipitated. The supernatant was removed, the solid washed with petroleum ether (3 x 50 cm^3), and dried in *vacuo* for 4 hours. The yellow powder had a variable composition, but Mg and Ti analyses may not have been reliable in this case as the insolubility of DIBP in aqueous solutions made analyses complicated. The solid did not dissolve cleanly in dilute sulphuric acid solutions, and a black suspension was formed when the solid was digested by concentrated sulphuric acid.

Reaction between $(PhO)_2TiCl_2$ and $MgCl_2$ in EtOAc

A solution of $(PhO)_2TiCl_2$ (4.86g, 12.0 mmol) in EtOAc (20 cm^3) was mixed with a solution of $MgCl_2$ in EtOAc (30 cm^3, 0.40 mol dm^{-3}, 12.0 mmol), and the resulting deep red solution was heated to 60°C with magnetic stirring for 4 hours. The solvent was removed by pumping and an oily solid was produced. This was heated to 80°C in *vacuo* for 4 hours, and a red powder resulted. This solid had a variable composition and the ^1H n.m.r. spectrum of its solution in $CDCl_3$ showed that very little EtOAc was present in comparison to $(PhO)_2TiCl_2$.

Reaction of $CpTiCl_3$ with $MgCl_2$ in EtOAc

A solution of $CpTiCl_3$ (0.23g, 1.05 mmol) in EtOAc (20 cm^3) was mixed with a solution of $MgCl_2$ in EtOAc (2.63 cm^3, 0.40 mol dm^{-3}, 1.05 mmol), and the resulting yellow solution was heated to 60°C with magnetic stirring for 2 hours. After cooling to room temperature the volume of the solution was reduced by pumping, and a precipitate formed when the volume of the solution had been reduced by approximately one half. The supernatant was removed, the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. The ^1H n.m.r. spectrum of the solid showed that cyclopentadienyl and EtOAc were present in the solid in the ratio 7:1 and the i.r. spectrum of the solid compared exactly with that of the EtOAc solvate of $MgCl_2$ in the carbonyl stretching region.

Reaction of $MeSnCl_3$ with $MgCl_2$ in EtOAc

A solution of $MeSnCl_3$ (0.30g, 1.25 mmol) in EtOAc (10 cm^3) was added to a solution of $MgCl_2$ in EtOAc (3.1 cm^3, 0.40 mol dm^{-3}, 1.25 mmol), and the resulting clear solution was heated to 60°C with magnetic stirring for 1 hour. No solid precipitated from this solution after standing at -20°C for 7 days so the solvent was removed by

pumping. An oily solid was produced, which proved intractable.

Reaction of Me_2SnCl_2 with $MgCl_2$ in EtOAc

Dimethyl tin dichloride, Me_2SnCl_2, was prepared by heating $SnMe_4$ (0.79 cm^3, 4.34 mmol) with $SnCl_4$ (0.50 cm^3, 4.34 mmol) to 120°C for 5 minutes. On cooling white crystals formed which were washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo*. (Yield 0.90g, 95%). The solid could be recrystallized unchanged from EtOAc.

A solution of Me_2SnCl_2 (1.0g, 4.55 mmol) in EtOAc (10 cm^3) was added to a solution of $MgCl_2$ in EtOAc (11.4 cm^3, 0.40 mol dm^{-3}, 4.55 mmol), and the resulting clear solution was heated to 60°C with magnetic stirring for 4 hours. The volume of the solution was reduced by approximately two-thirds, and a white precipitate formed. The supernatant was removed, the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. Only traces of EtOAc were observed in the ^1H n.m.r. spectrum of this solid in $CDCl_3$ solution and elemental analysis showed that only traces of Mg were present in the solid. The solid was redissolved in EtOAc (10 cm^3) and on standing for 14 days at room temperature white crystals were formed, which were

isolated as above. The ^1H n.m.r. and i.r. spectra of the crystals were identical to those of an authentic sample of Me_2SnCl_2.

Reaction of $TiCl_3$ with $MgCl_2$ in EtOAc

A green solution of $TiCl_3$ (1.50g, 9.72 mmol) in EtOAc (120 cm^3) was prepared by solvent extraction of $TiCl_3$ from a Soxhlet apparatus over 16 hours. This was added to a solution of $MgCl_2$ in EtOAc (24.3 cm^3, 0.40 mol dm^{-3}. 9.72 mmol), and the resulting green solution was heated to 60°C, with magnetic stirring, for 4 hours. The volume of the solution was reduced to approximately one-tenth of its original value by pumping, and on standing for 30 days a green crystalline precipitate formed. The supernatant was removed, the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 30 minutes. (Yield 0.25g, 5%). On standing over 30 days the green crystalline solid changed to a grey amorphous powder.

i.r.	1743(w)	1690(s)	1640(s)	1530(w)	1460(s)
	1400(w)	1380(s)	1310(s)	1280(s)	1240(m)
	1160(w)	1100(m)	1045(s)	1110(m)	850(m)
	850(w)	720(w)	640(w)	650(s)	465(m)
	400(s)	335(s)	240(s)	cm^{-1}	

Analysis based on $TiMgCl_5C_{12}H_{24}O_6$:

calculated:	Ti, 9.46;	Mg, 4.72%
found:	9.30	3.82

Preparation of $TiCl_3 \cdot 3EtOAc$

$TiCl_3$ (2.0g, 13.0 mmol) was extracted into EtOAc (120 cm^3) using a Soxhlet apparatus. The resulting green solution was concentrated to approximately one-fifth its original volume by pumping. On standing for 7 days green crystals formed. The supernatant was removed, the solid washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 10 minutes (Yield 0.81g, 15%). On standing over 7 days the green crystals decomposed to a grey powder.

i.r. 1640(s) 1465(s) 1380(m) 1320(m) 1290(w)
1100(w) 1040(m) 1010(m) 955(w) 845(m)
720(w) 650(w) 665(w) 465(m) 400(m)
350(s) 270(m) cm^{-1}

Analysis based on $TiCl_3C_{12}H_{24}O_6$:
calculated: Ti, 11.44%
found: 11.60

Reaction of VCl_3 with $MgCl_2$ in EtOAc

A solution of VCl_3 (2.0g, 12.7 mmol) in EtOAc (120 cm^3) was prepared by solvent extraction of VCl_3, using a Soxhlet apparatus over 16 hours. This purple solution was added to a solution of $MgCl_2$ in EtOAc (31.7 cm^3, 0.40 mol dm^{-3}, 12.7 mmol) and the resulting solution was heated to 60°C and

magnetically stirred, for 4 hours. The solvent was removed from this solution by pumping, but solid did not precipitate until almost all the solvent had been removed. The solid was washed with petroleum ether (2 x 50 cm^3) and dried in *vacuo* for 4 hours. The solid was inhomogenous and had a variable composition.

Analysis: V, 10.7; Mg, 8.7; C, 25.5; H, 4.7%

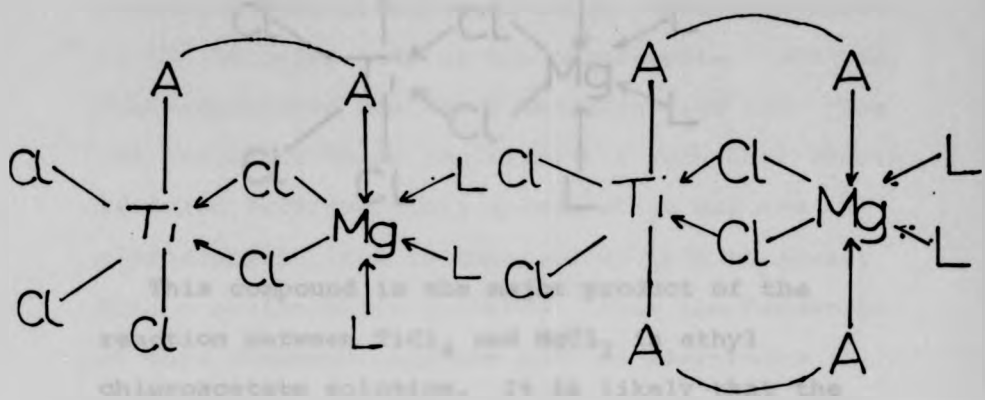
CHAPTER 3

3.0. Introduction

There is considerable current interest in compounds where two metals are involved in the same molecular compound. The metal atoms, which can be the same or different, may be linked either by a metal-metal bond, or via bridging groups. Interest arises from possible co-operative effects operating between the two metal atoms. This is particularly relevant to redox reactions, and for providing adjacent sites for the binding and activation of small molecules. It has been noted in Chapter 2 that such systems are relevant to this investigation [e.g. $MgCl_2 \cdot TiCl_4 \cdot 4EtOAc$, (I)].

The relative instability of the $MgCl_2$ bridge system in (I) has been discussed in Chapter 2, and this Chapter is concerned with the design and synthesis of related systems. If another group also bridged the magnesium and titanium atom the stability of the bimetallic unit would probably be increased. Since magnesium is utilizing its full valency in the $MgCl_2$ donor unit, a possible strategy would be to derive the further link from a suitable group on the titanium centre. If this group (say A-A) contains a suitable donor site, then this site could displace one, or more of the

existing donor (solvent) molecules on the magnesium. Possible models are shown below.



Several model compounds of the type (A-A) $TiCl_3$ or $(A\text{-}A)_2$ $TiCl_2$ are known, where (A-A) is a mono-anion which can co-ordinate in a bidentate mode. Suitable anions include acetylacetonate, carboxylate and nitrate, and a variety of specially constructed species could be envisaged. Carboxylates were chosen for this study because of their well established ability to bridge two metal centres[126], and because it has been shown that titanium carboxylates are produced when $TiCl_4$ is heated with esters in catalyst preparations[127]. When the structure of $MgCl_2 \cdot TiCl_3(O_2CCH_2Cl) \cdot 3EtO_2CCH_2Cl$ was reported[123], this confirmed that such a linkage could form a stable bridging system.

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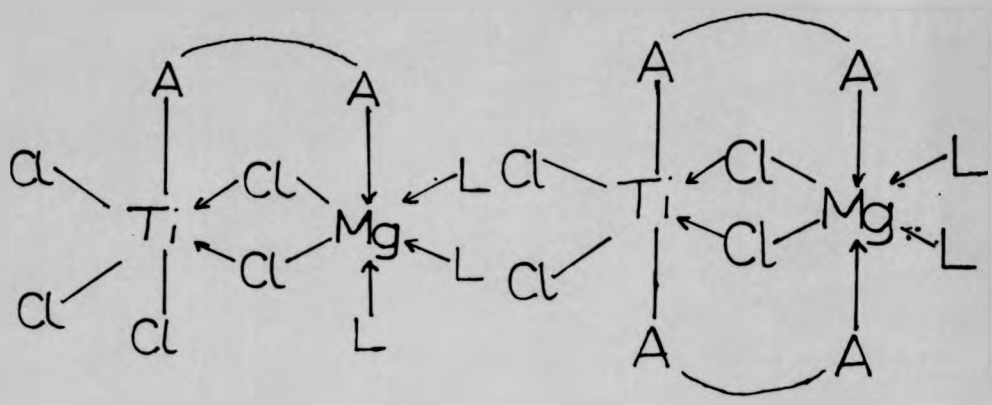
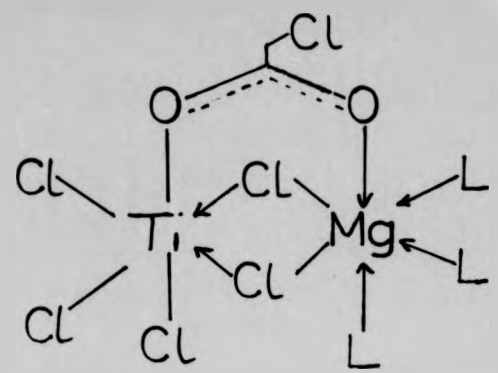
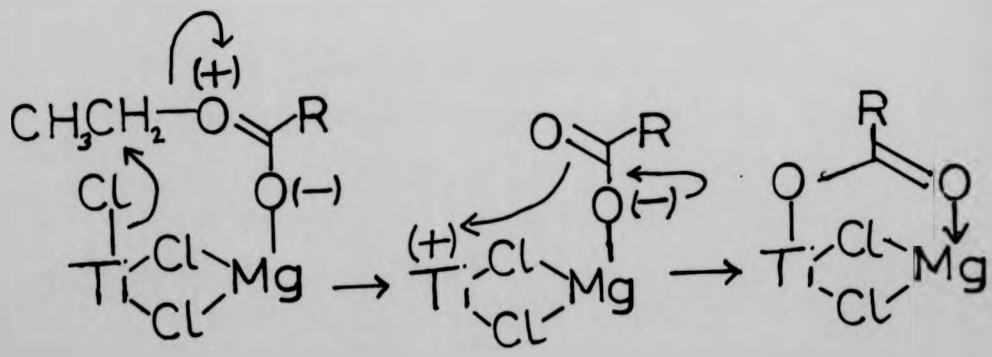


Several model compounds of the type (A-A) $TiCl_3$ or $(A\text{-}A)_2\ TiCl_2$ are known, where (A-A) is a mono-anion which can co-ordinate in a bidentate mode. Suitable anions include acetylacetonate, carboxylate and nitrate, and a variety of specially constructed species could be envisaged. Carboxylates were chosen for this study because of their well established ability to bridge two metal centres[126], and because it has been shown that titanium carboxylates are produced when $TiCl_4$ is heated with esters in catalyst preparations[127]. When the structure of $MgCl_2 \cdot TiCl_3(O_2CCH_2Cl) \cdot 3EtO_2CCH_2Cl$ was reported[123], this confirmed that such a linkage could form a stable bridging system.



This compound is the major product of the reaction between $TiCl_4$ and $MgCl_2$ in ethyl chloroacetate solution. It is likely that the carboxylate bridged system is derived from a complex which is isomorphous with (I), by a reaction in which the ethyl group of a chloro-ester is attacked by a chloride on titanium, and ethyl chloride is eliminated, as shown in the scheme below.

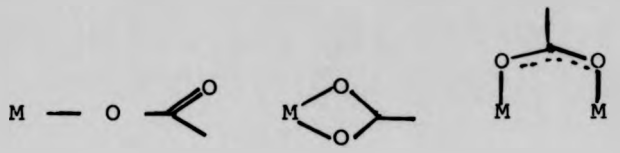


Since such a link is not produced in the EtOAc compound (I) the reaction probably takes place because of the combination of the inductive effect of the chlorine atom of the chloro-ester, and the electropositive nature of the magnesium ion. The net result of these two effects is such that charge is drawn from the ethyl group, which becomes electrophilic, and is then susceptible to attack from a nucleophilic chloride. Thus the formation of this compound requires special electronic properties in the substituents of the carboxylate group of the ester.

It became clear in the initial search for suitable titanium carboxylate compounds that the co-ordination chemistry of titanium chloro-carboxylates has not yet been studied in detail. Consequently much of this work involved the characterisation of the systems $TiCl_x(O_2CR)_{4-x}$ (x = 2 or 3) (R = alkyl or aryl) and an investigation of their properties and chemistry. During these investigations some titanium oxo-compounds were prepared, and the chemistry of such compounds will therefore also be discussed briefly.

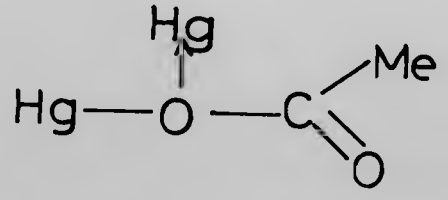
3.1. Carboxylate Groups as Ligands

The carboxylate group, RCO_2^-, is an interesting ligand because of its ability to co-ordinate to metal atoms in many different ways. The common modes of carboxylate co-ordination are shown below.

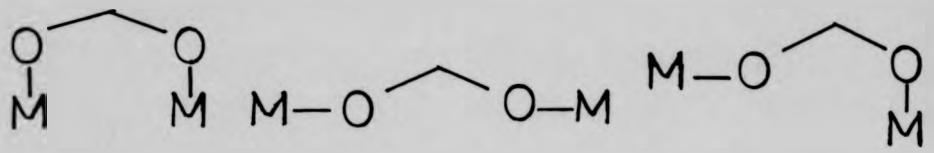


unidentate bidentate bridging

There are many variations on these three basic models which have been discussed by Waddington *et al*[128], and some compounds contain more than one type of carboxylate. For example, simple unidcntate co-ordination of acetate has been identified in the compound $Ph_3Sb(O_2CMe)_2$[129], while in the compound $Hg(O_2CMe)_2P(C_6H_{11})_3$[130] the acetate is also "unidentate", but co-ordinates to two metal atoms, as shown below.



Several types of bridging carboxylates have been identified by X-ray methods. The most common type of co-ordination is *syn-syn*, which is found in $[Os(O_2CMe)(CO)_3]_2$ [131], and compounds containing metal-metal bonds such as $[Cr(O_2CMe)\cdot H_2O]_2$ [132]. However, *anti-anti* co-ordination is found in $Mn(O_2CMe)_2\cdot 4H_2O$ [133], and there is *syn-anti* co-ordination of a carboxylate in $Cu(O_2CH)_2$ [134].



A review by Deacon and Phillips[135] describes all the metal carboxylates which have been structurally characterised by X-ray methods up to 1980, and attempts to correlate the mode of co-ordination with the difference in stretching frequencies between the symmetric and assymetric modes of the carboxylates observed in their i.r. spectra, called Δ, so $\Delta \approx (\nu_{assym} - \nu_{sym})cm^{-1}$.

Unidentate co-ordination occurs when only one of

the two oxygens of the carboxylate group co-ordinates to a metal. In effect a pseudo-ester is formed, and $\nu_{sym}(CO_2)$ is decreased and $\nu_{assym}(CO_2)$ is increased, relative to the free carboxylate ion, taken as the sodium or potassium salts where Δ is 164 cm^{-1}. Thus values of Δ are generally much larger than 164 cm^{-1} if co-ordination is unidentate. Values of Δ for monodentate carboxylates vary between 150 and 300 cm^{-1}.

When a carboxylate is bidentate, or chelating, Δ is often lower than in ionic compounds, typical values being between 65 and 170 cm^{-1}. This is also the case when a carboxylate bridges two metal centres, where typical values of Δ are between 120 and 170 cm^{-1}. It is therefore difficult to distinguish between these two modes of co-ordination on the basis of evidence from i.r. spectra, though a very low value of Δ has been proposed to be indicative of chelating rather than bridging co-ordination[135].

Hence while the assignments of the structure of carboxylate complexes based only on evidence from i.r. spectroscopy are far from definitive, nevertheless in the absence of X-ray data i.r. spectroscopy often does give some indication of the bonding mode.

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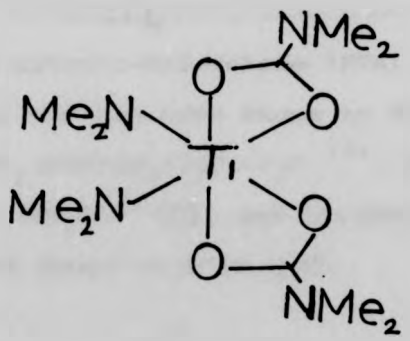
Hence while the assignments of the structure of carboxylate complexes based only on evidence from i.r. spectroscopy are far from definitive, nevertheless in the absence of X-ray data i.r. spectroscopy often does give some indication of the bonding mode.

3.2. The Preparation and Properties of Titanium(IV) Carboxylates

Few carboxylates of titanium, other than organometallic compounds containing the cyclopentadienyl ligand which are discussed in Section 3.3., have been structurally characterised by X-ray methods.

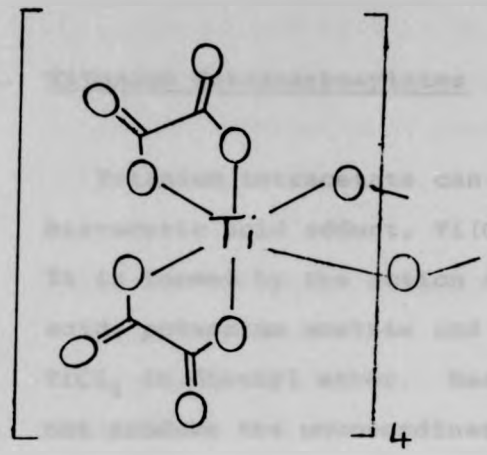
The compound $Ti(NMe_2)_2(O_2CNMe)_2$, which is formed by the action of CO_2 on $Ti(NMe_2)_4$, is a simple monomer with six co-ordinate titanium atoms and chelating carboxylate groups[136].



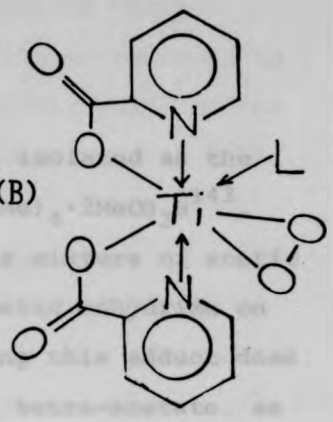
Other titanium carboxylates which have been structurally characterised contain multifunctional carboxylates including oxalate, pinacolate (o-$C_5NH_4CO_2^-$), and nitrilotriacetate [$N(CH_2CO_2)_3^{3-}$]. Thus chelating oxalates are found in the tetrameric oxo-compound $([NH_4]_2[TiO(C_2O_4)_2\cdot H_2O])_4$ [137](A). The multifunctional carboxylates containing nitrogen donors, especially pinacolate, have been used to

stabilize seven co-ordinate titanium peroxo compounds such as $Ti(O_2)(C_5NH_4CO_2)_2 \cdot HMPA$[138] (B) and $[Ti(O_2)(C_5NH_4CO_2)_2(H_2O)_2] \cdot 2H_2O$ [139,140].

(A)

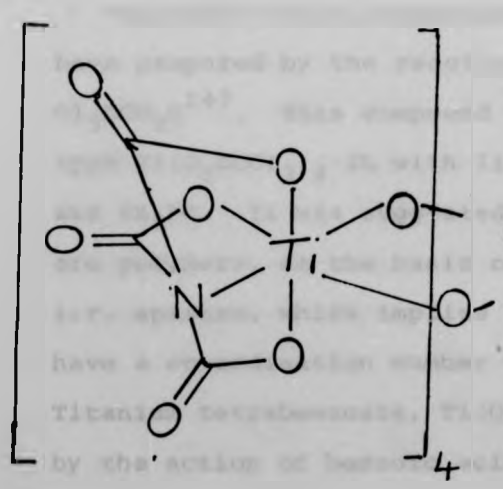


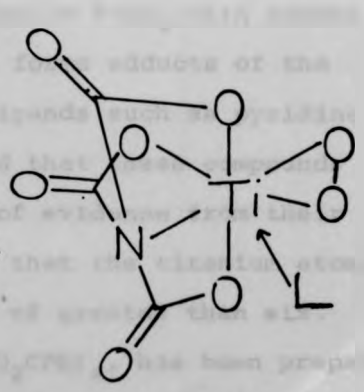
(B)



The ligand nitrilo-triacetate (NTA) is similar to pinacolate, and has been shown to form compounds such as $Na_4[Ti_2(NTA)\cdot(O_2)]_2O \cdot H_2O$ [141], and tetrameric $Cs_4[TiO(NTA)]_4 \cdot 6H_2O$[142] (C), and [Ti(NTA)$(O_2)$L] (D) L = monodentate donor such as HMPA.

(C)

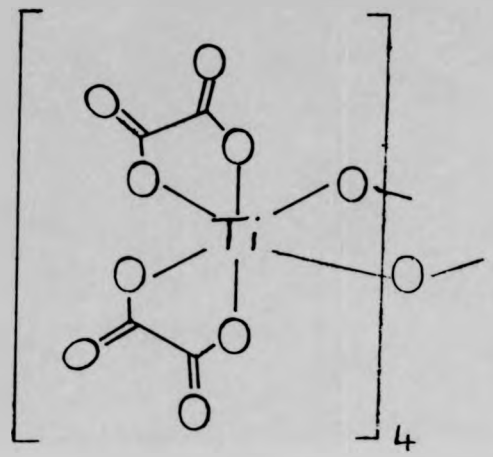




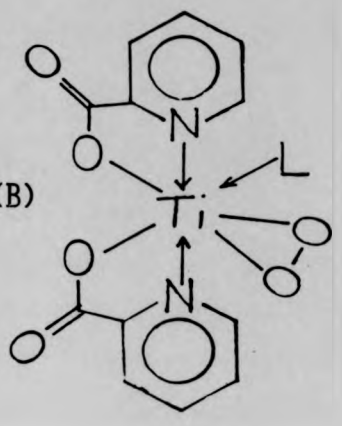
(D)

stabilize seven co-ordinate titanium peroxo compounds such as $Ti(O_2)(C_5NH_4CO_2)_2 \cdot HMPA$[138] (B) and $[Ti(O_2)(C_5NH_4CO_2)_2(H_2O)_2] \cdot 2H_2O$ [139,140].

(A)



(B)



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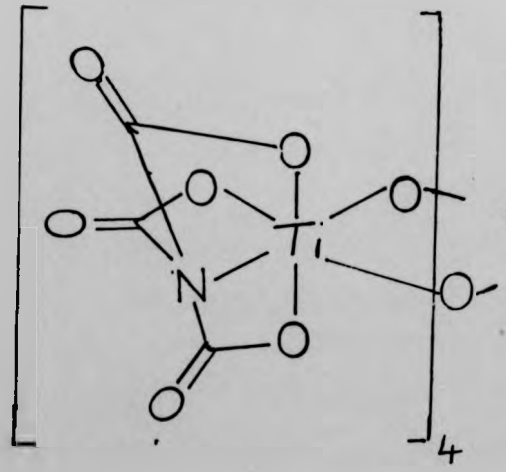
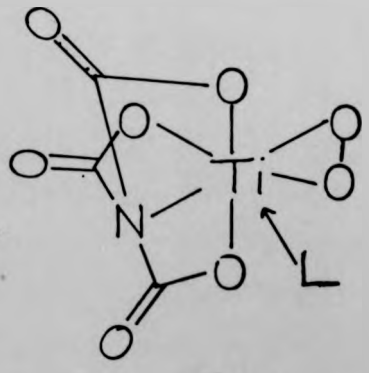
(C)





(D)

However, the titanium compounds of simple carboxylates such as acetate, and its derivatives, have yet to be structurally characterised.

3.2.1. Titanium Tetracarboxylates

Titanium tetracetate can be isolated as the bis-acetic acid adduct, $Ti(O_2CMe)_4 \cdot 2MeCO_2H$[143]. It is formed by the action of a mixture of acetic acid, potassium acetate and acetic anhydride on $TiCl_4$ in diethyl ether. Heating this adduct does not produce the unco-ordinated tetra-acetate, as oxo compounds, such as $TiO(O_2CMe)_2$, are formed[144,145]. This compound has not been structurally characterised but is likely to be polymeric with bridging oxygen atoms. Under less severe conditions the co-ordinated acetic acid is not lost[146].

The tetra(trichloroacetate), $Ti(O_2CCCl_3)_4$, has been prepared by the reaction of $TiCl_4$ with excess Cl_3CCO_2H[147]. This compound forms adducts of the type $Ti(O_2CCCl_3)_4 \cdot 2L$ with ligands such as pyridine and Ph_3PO. It was suggested that these compounds are polymers, on the basis of evidence from their i.r. spectra, which implies that the titanium atoms have a co-ordination number of greater than six. Titanium tetrabenzoate, $Ti(O_2CPh)_4$, has been prepared by the action of benzoic acid on $TiCl_4$. It was

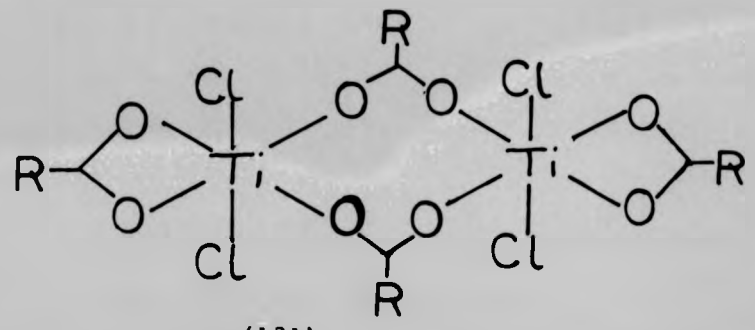
proposed that the larger anions do not allow the co-ordination of further ligands[143].

It is not simple to rationalize the behaviour of the tetracarboxylates in terms of their structure, and clearly X-ray data is required to establish unambiguously the bonding modes of the carboxylate group(s) in these compounds.

3.2.2. Titanium Chloro Bis-Carboxylates

Compounds of the type $TiCl_2(O_2CR)_2$ have been prepared by the action of an excess of the appropriate acid on $TiCl_4$[145, 148, 149]. The temperature of the reaction mixture has to be carefully controlled or further reaction takes place, and oxo compounds of the type $TiO(O_2CR)_2$ are the final products. Tris-carboxylates of the type $TiCl(O_2CR)_3$ are unknown.

On the basis of spectroscopic evidence Amaudrut *et al*[150,151] have suggested that compounds of the type $TiCl_2(O_2CR)_2$ are dimeric, and contain two different types of carboxylate groups, one bridging two titanium centres, and one bidentate on one titanium centre.



(131)

The evidence for this structure lies in three bands which are observed in the i.r. spectra of a large series of compounds of the type $TiX_2(O_2CR)_2$ (X = Cl, Br; R = alkyl or chlorinated alkyl). Since a carboxylate group has only two i.r. active stretches associated with it, it was therefore proposed that these compounds contain two types of carboxylate, two bands accidentally overlap and consequently only three bands in all are observed.

Evidence from the Raman spectra of the compounds suggests that the halogen atoms are trans to one another[151]. This proposal is substantiated by this work, which will be discussed in Section 3.15.

3.2.3. Titanium Chloro Mono-Carboxylates

Amaudrut and his co-workers also studied compounds of the type $TiCl_3(O_2CR)$[145]. These compounds are prepared by adding the pure acid to a large excess of $TiCl_4$, a method originally described by Mehotra[148].

When the yellow acetate $TiCl_3(O_2CMe)$, produced by this method is heated to between 75 and 100°C for 10 - 30 hours it changes form. Evidence for this change in form comes from the i.r. and X-ray powder spectra of the two types of the compound.

The i.r. spectrum of the unheated form, called A, has clearly resolved bands at 1610, 1490, and

1395 cm^{-1}, whereas the product of heating, form B, has a less well resolved spectrum with broad bands centred at 1480 and 1410 cm^{-1}. It was concluded that there was insufficient evidence to allow the structures the two forms of $TiCl_3(O_2CMe)$ to be assigned, though the presence of three bands in the spectrum of form A indicates that two different types of carboxylate are probably present in this case.

Form B of the mono-acetate can also be prepared by the action of an excess of $TiCl_4$ on $TiCl_2(O_2CMe)_2$.

The reactions of $TiCl_4$ with carboxylic acids in organic solvents, such as heptane, benzene, and dichlorobenzene, have been studied by i.r. and ^1H n.m.r. spectroscopy, in relation to the action of these systems as Freidel-Crafts catalysts[152].

The i.r. spectrum of a solution of a 1:1 molar ratio of $TiCl_4$ and $MeCO_2H$ showed that no unreacted acid is present immediately after mixing. Two carbonyl bands at 50 and 150 cm^{-1} lower than the carbonyl stretching frequency of the free acid (1760 cm^{-1}) were observed. These were assigned to the acetic acid adduct of $TiCl_4$, and the carboxylate which is produced by the elimination of HCl, respectively. Evolution of HCl is observed immediately on mixing and the band due to the adduct quickly losses intensity as the carboxylate forms,

though even after a prolonged reaction time some adduct remains unreacted.

$$TiCl_4 + MeCO_2H \rightarrow TiCl_4 \leftarrow O = \overset{OH}{\overset{|}{C}}Me$$

$$\downarrow$$

$$TiCl_3(O_2CMe) + HCl$$

When stronger acids such as CF_3CO_2H were studied it was found that free acid remained in solution even after extended reaction times. No adduct was observed as acid which did co-ordinate to $TiCl_4$ reacted immediately to produce the carboxylate.

$$TiCl_4 + CF_3CO_2H \rightarrow TiCl_3(O_2CCF_3) + HCl$$

The carboxylates, $TiCl_3(O_2CR)$ (R = Me, CF_3), were not isolated and identified, their presence was inferred simply from the spectroscopic data.

3.2.4. Reactions of the Compounds $TiCl_x(O_2CR)_{4-x}$ (x=2,3)

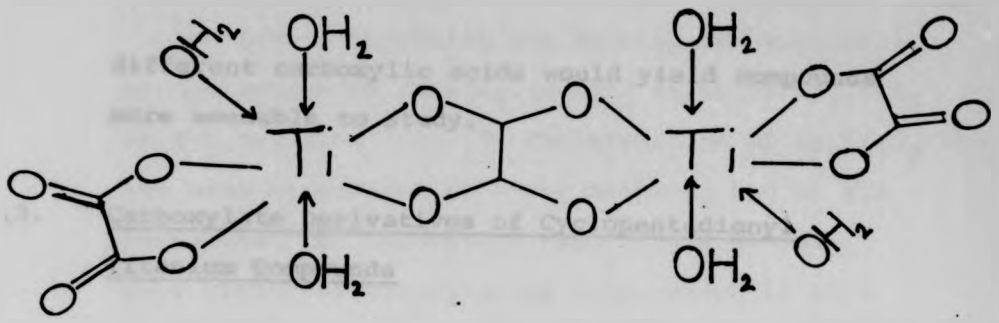
Few reactions of the compounds $TiCl_x(O_2CR)_{4-x}$ (x = 2 or 3) have been reported. These compounds decompose in $POCl_3$ to form the known compound $TiOCl_2 \cdot 2POCl_3$[153, 154], and the reactions of NOCl with $TiCl_3(O_2CMe)$ and $TiCl_2(O_2CMe)_2$ have also been

investigated[155]. Vapour pressure measurements indicate that the bis-acetate does not form an addition compound, but a 1:1 adduct forms in the reaction between NOCl and $TiCl_3(O_2CMe)$. On the basis of this evidence it was proposed that the titanium atoms are co-ordinatively saturated in $TiCl_2(O_2CMe)_2$, and hence have a co-ordination number of six.

As NOCl co-ordinates to $TiCl_3(O_2CMe)$ this suggests that either the titanium atoms are five co-ordinate in this compound, or that it contains titanium atoms which are six co-ordinate by virtue of a weak linkage such as a chloro-bridge, which is easily disrupted by NOCl.

3.2.5 Preparation and Properties of Titanium(III) Carboxylates

Two titanium (III) oxalate compounds $Ti_2(C_2O_4)_3 \cdot 10H_2O$ and $Cs[Ti(C_2O_4)_2(H_2O)_3] \cdot 2H_2O$ have been structurally characterised by X-ray methods. The former compound was shown to be dimeric with a bridging oxalate. There is pentagonal bipyramidal co-ordination of the seven co-ordinate titanium atoms[156]. The latter compound has a similar structure, except that it does not have bridging oxalates, and is thus monomeric[157].



A series of compounds with the formulae $TiCl_2(O_2CMe)$, $TiCl(O_2CMe)_2$ and $TiCl_2(O_2CMe)\cdot MeCO_2H$ have been prepared by the action of acetic acid on $TiCl_3$ in acetic anhydride solution.

$$TiCl_3 + MeCO_2H \xrightarrow{(MeCO)_2O} TiCl_2(O_2CMe) + HCl$$

A tris-carboxylate could not be isolated. All three solids were found to be insoluble in organic solvents, and polymeric structures were suggested on the basis of evidence from magnetic susceptibility measurements[158].

The authors of this work suggested that the substitution of acetate for chloride may be continuous, so that unique phases may not be formed, and the analytical data for the formulations given above were fortuitous.

The extreme insolubility of these compounds makes them difficult to investigate, though perhaps

different carboxylic acids would yield compounds more amenable to study.

3.3. Carboxylate Derivatives of Cyclopentadienyl Titanium Compounds

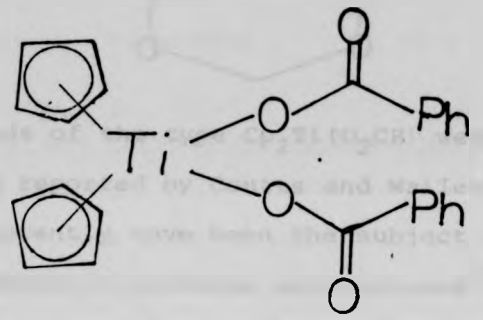
A brief discussion of cyclopentadienyl titanium carboxylates is included here because several of these derivatives containing simple carboxylate groups have been structurally characterised. This is in direct contrast to the non-organometallic compounds, so these compounds serve as models for compounds prepared in this work.

The mono-cyclopentadienyl titanium(iV) carboxylates can be prepared by displacement of chloride from $CpTiCl_3$ ($Cp = \eta^5\text{-}C_5H_5$) by the silver or potassium salt of the appropriate acid in THF solution[159].

$$CpTiCl_3 + 3Ag(O_2CR) \rightarrow CpTi(O_2CR)_3 + 3AgCl$$

The benzoate can also be prepared by the action of benzoyl peroxide on $Cp_2Ti(C_6H_5)_2$[160]. On the basis of evidence from infra-red spectroscopy this group of compounds was assigned a structure in which the titanium atom has pseudo-tetrahedral co-ordination, with the carboxylate groups being unidentate[159].

The bis-carboxylates can be prepared similarly by the action of carboxylic acid salts on Cp_2TiCl_2 in THF solution[161, 162]. The structure of $Cp_2Ti(O_2CPh)_2$ has been determined by X-ray methods, and it was found that two unidentate carboxylate groups co-ordinate to the titanium atom, which is in a pseudo-tetrahedral environment[162].

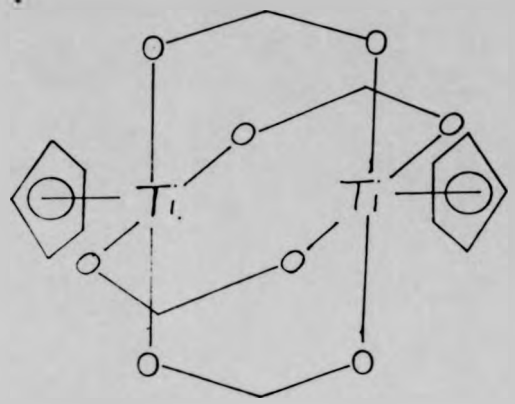


Titanium(III) cyclopentadienyl bis-carboxylates can be prepared either by the action of a salt of the appropriate acid on $CpTiCl_2$ in THF solution, or by the action of the acid itself on $CpTiCl_2$ in the presence of a base such as triethylamine[163].

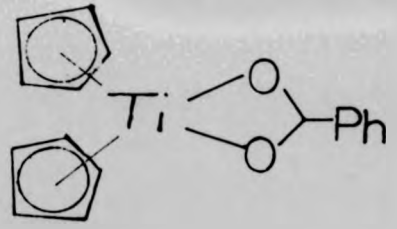
$$CpTiCl_2 + 2RCO_2H + 2Et_3N \rightarrow CpTi(O_2CR)_2 + 2Et_3NHCl$$

A dimeric structure with four carboxylate groups bridging two titanium atoms has been proposed on the basis of evidence from E.S.R. and i.r. spectra of these compounds, and confirmed when the structure

of Cp $Ti(O_2CPh)_2$ was determined by X-ray methods[164].



Compounds of the type $Cp_2Ti(O_2CR)$ were originally reported by Coutts and Wailes[165], but more recently have been the subject of the study of magnetic exchange interactions[166]. During the course of these studies the structure of $Cp_2Ti(O_2CPh)$ was determined by X-ray methods, and was shown to contain a tetrahedrally co-ordinated titanium atom, and bidentate carboxylate groups[167]. This type of co-ordination was also found in the compound $Cp_2Ti(O_2CCMe_3)$[168] and in complexes of bifunctional acids which link two titanium centres, in compounds of the type $Cp_2Ti(O_2C(C_xH_y)CO_2)TiCp_2$[167].



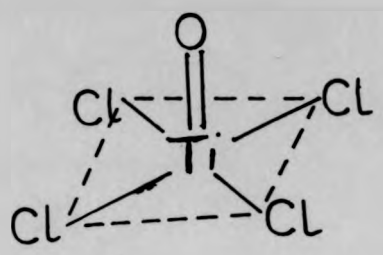
The correlation of the structure of cyclopentadienyl titanium carboxylates with Δ values obtained from their i.r. spectra is shown below.

Compound	Co-ordination mode	$\Delta(cm^{-1})$	Ref.
$CpTi(O_2CR)_3$	unidentate	~ 280	160
$Cp_2Ti(O_2CR)_2$	unidentate	> 300	161
$CpTi(O_2CR)_2$	bridging	150-180	163
$Cp_2Ti(O_2CR)$	bidentate	60-110	165

3.4. Preparation and Properties of Titanium Oxo-Compounds

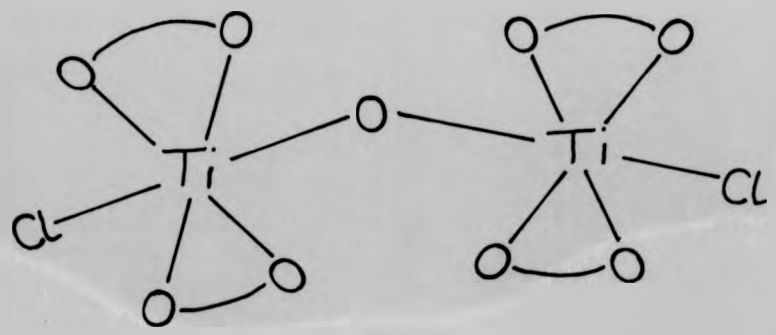
Titanium has a high affinity for oxygen, as demonstrated by the air reactivity of many of its compounds. Hence compounds with titanium-oxygen bonds are formed by hydrolysis reactions, or in aqueous solution. These compounds are usually polymeric with oxygen bridges between titanium atoms, as previously discussed in Chapter 1.

However, discrete Ti-O units have been identified unambiguously by X-ray methods in the compounds $[R_4N]_2[TiOCl_4]$ (R = Me, Et)[17,169], and in a titanium porphyrin complex[19]. In all three cases the titanium atoms were determined to be just above the centre of a plane of four ligand atoms , and the oxygen makes the apex of a square-based pyramid.



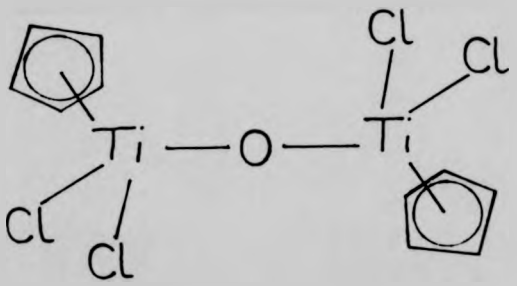
A band at 975 cm^{-1} in the i.r. spectra of the compounds $[R_4N]_2[TiOCl_4]$ was proposed to be associated with the Ti-O stretching mode in these compounds, and similar bands have been suggested to be diagnostic of the presence of the Ti-O unit in other compounds[18].

In most cases oxygen atoms bridge between two titanium atoms to form dimeric or polymeric compounds. Partial hydrolysis of $Ti(acac)_2$ $CHCl_3$ solution produces crystals of $[TiCl(acac)_2]_2O \cdot CHCl_3$. The structure of this compound, as determined by X-ray methods, contains an oxygen which bridges two titanium atoms in a discrete molecular dimer[170].

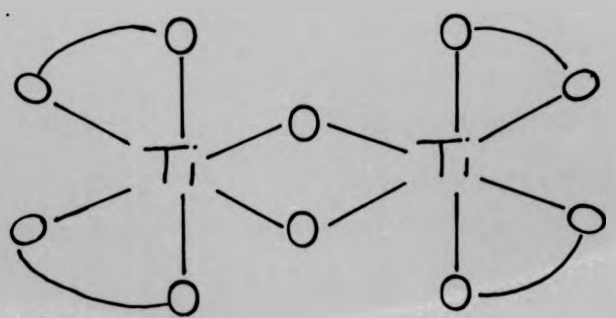


The Ti-O-Ti, angle was determined to be 167.5^{o}, which suggests that there is significant double bond character in the titanium oxygen linkages. This arises from π-donation of non-bonding oxygen 2p electrons into vacant d orbitals on titanium.

This type of near linear bridge was also found in the dimeric peroxo compound $Na_4[Ti(NTA)(O_2)]_2O \cdot 11H_2O$[141], and in the cyclopentadienyl derivatives $(CpTiCl_2)_2O$[171], and $(Cp_2TiCl)_2O$[172], using X-ray methods.

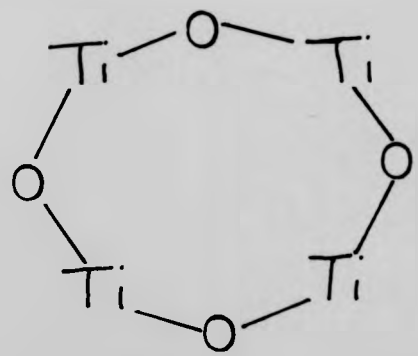


Further hydrolysis of $Ti(acac)_2Cl_2$ produces $[TiO(acac)_2]_2$. The structure determination of this compound by X-ray methods revealed that it contains a double oxygen bridge[173].



Two titanium atoms and two oxygen atoms form a planar four membered ring, in which the Ti-O-Ti angle was found to be 96.6°, and the O-Ti-O angle 83.4°.

Tetrameric compounds containing eight membered titanium-oxygen rings, such as $[NH_4][TiO(C_2O_4)_2H_2O]$[137], $Cs_4[TiO(NTA)]_4 \cdot 6H_2O$[142], and $[(C_5H_4Me)Ti(Cl)O]_2$[174], have also been characterised by X-ray methods. The Ti-O-Ti angles in these compounds are between 140° and 170°, so this also suggests some double bond character in the titanium-oxygen linkages.



It can be concluded from these cases that where structures have been determined by X-ray methods there is an apparent tendency for oxygen bridged species to form in the hydrolysis reactions of titanium compounds. The observation that Ti-O-Ti angles tend towards 180° when there are no other steric requirements in the molecule suggests that

the Ti-O linkages in these compounds have significant double bond character.

In more fully hydrolysed compounds tetramers containing eight membered titanium-oxygen rings are often formed, rather than dimers, because it is possible to have larger Ti-O-Ti angles, which allow greater p_π - d_π orbital overlap, and hence a higher bond order.

3.5. Results and Discussion

A representative group of three compounds of the type $TiCl_3(O_2CR)$ has been studied. The carboxylate acids chosen for study were

(i) acetic acid, because the products of its reactions with $TiCl_4$ have been partially characterised.

(ii) benzoic acid, because of the relevance of benzoates to propylene polymerisation catalysts.

(iii) trimethyl acetic acid, because it was considered that a tertiary butyl alkyl group would enhance the solubility of the compounds, as proved to be the case.

3.6. Preparation of the Compounds $TiCl_3(O_2CR)$

The mono-acetate, $TiCl_3(O_2CMe)$, was prepared as previously reported[149], by adding dry acetic acid dropwise to a stirred excess of neat $TiCl_4$ at 0^oC. There was vigorous evolution of HCl gas, and a yellow solid precipitated from the red solution.

$$TiCl_4 + MeCO_2H \rightarrow TiCl_3(O_2CMe) + HCl$$

The supernatant was removed, and the yellow solid was washed with petroleum ether until the washings were clear, and then dried in *vacuo*. The amorphous yellow powder which resulted consistently analysed as being high in chloride, and this along with extreme air reactivity of the solid suggested the presence of a large amount of unreacted $TiCl_4$.

When acetic acid was added to a stirred solution of $TiCl_4$ in CH_2Cl_2 in a 2:1 ratio of $TiCl_4$:$MeCO_2H$ evolution of HCl was still observed. In this case precipitation of the solid was not immediate, but yellow microcrystals formed on stirring at room temperature for 16 hours. The solid, which analysed as $TiCl_3(O_2CMe)$, could be recovered by removing the supernatant liquid,

washing with petroleum ether, and drying in *vacuo*. The i.r. spectrum of the product is very similar to that previously reported[149], except that a band at 498 cm^{-1}, which could have been due to $TiCl_4$ impurity is not observed in the present sample.

Benzoic acid proved much less reactive than acetic acid, in that the product of its reactions with either neat $TiCl_4$ or solutions in CH_2Cl_2, or benzene, consistently contained unreacted acid. This was detected in the i.r. spectra of the yellow solid products which always contained a band at 1700 cm^{-1}, due to the carbonyl stretch of benzoic acid. The most satisfactory method for the preparation of $TiCl_3(O_2CPh)$ is to add two mole equivalents of $TiCl_4$ to a toluene solution of $PhCO_2H$. Heating the resulting yellow suspension to 100°C results in the solid dissolving in the red solution. On cooling to room temperature a fine yellow precipitate forms under the red solution. The solid was isolated by washing with petroleum ether until the washings were clear, and drying in *vacuo*.

This method is also suitable for the preparation of $TiCl_3(O_2CCMe_3)$ from $TiCl_4$ and solid Me_3CCO_2H, but in this case the increased solubility of the product means precipitation of the solid only takes place on standing at -20°C. Yellow crystals are

produced which can be recrystallized from a minimum volume of benzene.

3.7. Infra-Red Spectra of the Compounds $TiCl_3(O_2CR)$

The i.r. spectra of all the mono-carboxylates were similar in the carboxylate stretching region, except that the spectrum of the benzoate is complicated by the presence of absorptions due to the phenyl ring.

Bands in the spectrum of $TiCl_3(O_2CMe)$ are observed at 1590, 1540, 1470, 1445, 1405 and 1380 cm^{-1}. In some samples a weak band at 1655 cm^{-1} was observed and probably arises from some bis-acetate impurity, as a strong band at 1650 cm^{-1} is observed in the spectrum of $TiCl_2(O_2CMe)_2$. The absorptions at 1470, 1445 and 1380 cm^{-1} are significantly less intense when the sample is made up as a mull in hexafluorobutadiene as opposed to nujol. These bands are therefore assigned as C - H stretching modes, and they do not appear to obscure any carboxylate bands. Therefore three bands in the spectrum at 1590, 1540 and 1405 cm^{-1} may be assigned to carboxylate [$\nu(CO_2)$] stretching modes. Three bands at 1590, 1540 and 1405 cm^{-1} in the spectrum of $TiCl_3(O_2CCMe_3)$ may be similarly assigned.

The spectrum of $TiCl_3(O_2CPh)$ shows bands at 1600, 1555, 1500 and 1410 cm^{-1}. Since the band at 1500 cm^{-1} is absent in the spectra of the other carboxylates this may reasonably be assigned to a phenyl ring stretch, as, in part, may the absorption at 1600 cm^{-1}.

As discussed previously, one carboxylate group has only two i.r. active stretches [$\nu(CO_2)_{assym}$ or $_{sym}$] associated with it, thus if all three bands identified above arise from carboxylate stretching modes then it appears that compounds of the type $TiCl_3(O_2CR)$ must contain two different types of carboxylate group.

It is difficult to assign these bands satisfactorily, but some general conclusions may be drawn. The maximum value of Δ for the present compounds is 190 cm^{-1}, and by comparison with other structurally characterised carboxylates[135], and titanium compounds in particular[160], it would seem unlikely that the monocarboxylates contain unidentate carboxylate groups. The Δ value is usually of the order of 300 cm^{-1} in such cases. This further illustrates the fact that it is very difficult to distinguish between chelating and bridging carboxylates from i.r. spectroscopic evidence. In the present compounds three alternative Δ values of 190, 140 and 50 cm^{-1} could be consistent with either mode.

It seems likely that an X-ray study will be required to assign unambiguously the structure of compounds of the type $TiCl_3(O_2CR)$.

3.8. Reactions of the Compounds $TiCl_3(O_2CR)$

All of the titanium mono-carboxylates react with air, the yellow carboxylates become white powders within approximately 15 minutes of exposure. They are all soluble without apparent change in chlorinated solvents, but only $TiCl_3(O_2CCMe_3)$ is at all soluble in benzene, or toluene, at room temperature.

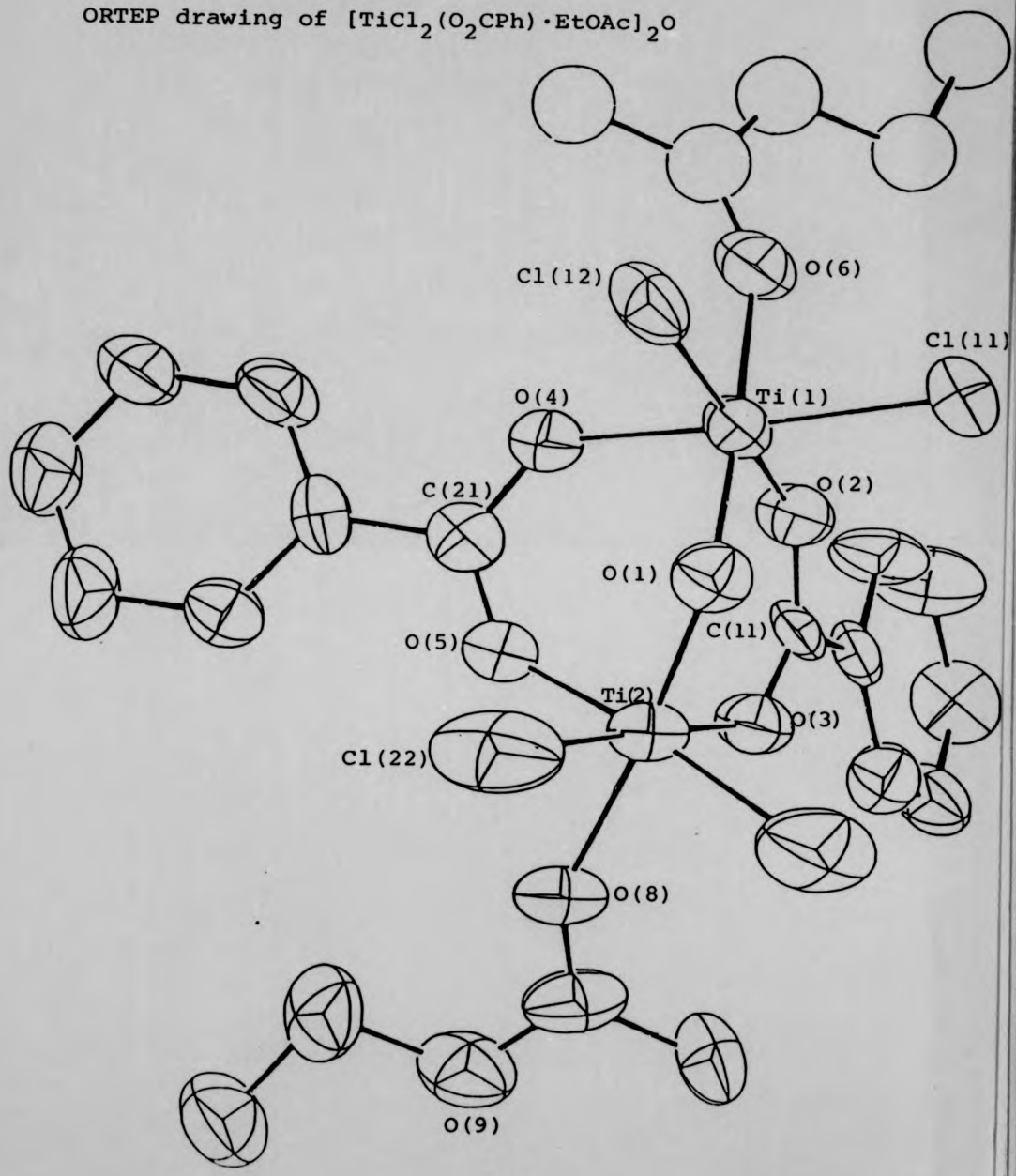
None of the three carboxylates studied dissolve in dry co-ordinating solvents such as EtOAc or THF. However, it was noticed that these compounds did dissolve to give clear yellow solutions, which slowly deposit yellow solids, when these solvents were not rigorously dry. These solutions, and the solids isolated from them, were studied in an attempt to define the reactions involved, and to characterise the products which appeared to arise from hydrolysis of the mono-carboxylates.

Controlled hydrolysis of the compounds was brought about by adding measured amounts of water to suspensions of the compounds $TiCl_3(O_2CR)$ in either EtOAc or THF which had been previously dried.

The solids dissolved to give clear solutions, and on standing yellow crystals formed in high yield. They could be isolated by removal of the solvent, washing with petroleum ether, and drying in *vacuo*.

Analysis of these solids shows them to be compounds of the type $[TiCl_2(O_2CR)\cdot L]_2O$ (R = Me, CMe_3, Ph; L = EtOAc, THF). The crystal structures of $[TiCl_2(O_2CPh)\cdot L]_2O$ (L = THF(III), EtOAc(IV)) were determined by X-ray methods. The compounds were shown to be isomorphous, and virtually isostructural. The titanium atoms in the dimer are bridged by two benzoate groups and an oxygen atom, which was derived from the added water. The co-ordination around the two metal atoms is near octahedral. The Ti-O-Ti angle is 137.4°, so the deviation from the ideal value of 180°, found in $(CpTiCl_2)_2O$[171] and $(Cp_2TiCl)_2O$[172], must be due to steric constraints placed on the system by the carboxylate bridges. As a consequence the Ti-Ti distance of 3.31Å is relatively short for a system of this type. The (carboxylate) C - O - Ti angles (133.2°) are somewhat larger than the ideal 120°, but this still allows a stable half-chair six membered ring ($\overbrace{\mu\text{-O) - Ti - O - C(R) - O - Ti}}$. The μ-oxo atom makes an angle of near 135° with both planes containing the two titanium atoms, and one of

ORTEP drawing of $[TiCl_2(O_2CPh)\cdot EtOAc]_2O$



CRYSTALLOGRAPHIC DATA

Crystal Data. $C_{22}H_{26}Cl_4O_{10}Ti_2$. Monoclinic, $P2_1/C$, a = 15.156(2), b = 14.405(4), c = 13.731(3)Å , β = 92.74(1)°. Z = 4.. R = 0.052 for 1690 observed ($I/\sigma(I) \geq 3.0$) diffractometer - collected reflections.

One ethyl acetate group is almost entirely disordered, and for clarity in the figure is replaced by a model ligand corresponding to the other group.

Average dimensions: Ti–Cl 2.266(4), Ti–μ–O(I)(μ–oxo) 1.783(7), Ti–O (carboxylate) 2.014(7) Ti–O(ligand) 2.090(7), C–O(acid) 1.272(8)Å; Ti(1)–O(1)–Ti(2)137.2(4), O(1)–Ti–O(ligand) 169.0(3), C–O–Ti 133.2(6), O–C–O(carboxylate) 123.3(9), Cl–Ti–O(carboxylate)[*trans*]169.8 (2)°. Compound (III) is isomorphous and virtually isostructural .

BOND LENGTHS (A)

TI(1)-CL(11)	2.271(3)	TI(1)-CL(12)	2.278(4)
TI(1)-O(1)	1.778(7)	TI(1)-O(2)	2.002(7)
TI(1)-O(4)	2.037(7)	TI(1)-O(6)	2.076(7)
TI(2)-CL(21)	2.256(4)	TI(2)-CL(22)	2.258(5)
TI(2)-O(1)	1.788(7)	TI(2)-O(3)	2.012(7)
TI(2)-O(5)	2.005(7)	TI(2)-O(8)	2.103(7)
O(2)-C(11)	1.284(12)	O(3)-C(11)	1.266(12)
O(4)-C(21)	1.268(12)	O(5)-C(21)	1.271(12)
O(6)-C(322)	1.033(30)	O(6)-C(331)	1.457(32)
O(7)-C(311)	1.536(22)	O(7)-C(321)	0.703(30)
O(7)-C(322)	1.229(34)	O(7)-C(331)	1.195(37)
O(8)-C(41)	1.241(13)	O(9)-C(41)	1.315(15)
O(9)-C(43)	1.538(15)	C(11)-C(12)	1.495(14)
C(12)-C(13)	1.400(15)	C(12)-C(17)	1.361(15)
C(13)-C(14)	1.374(15)	C(14)-C(15)	1.343(16)
C(15)-C(16)	1.379(17)	C(16)-C(17)	1.387(17)
C(211-C(22)	1.474(14)	C(22)-C(23)	1.369(15)
C(22)-C(27)	1.385(15)	C(23)-C(24)	1.377(16)
C(24)-C(25)	1.355(18)	C(25)-C(26)	1.371(20)
C(26)-C(27)	1.374(16)	C(311)-C(322)	1.707(30)
C(311)-C(35)	1.851(17)	C(321)-C(322)	1.326(39)
C(321)-C(331)	0.859(41)	C(321)-C(332)	1.727(49)
C(321)-C(342)	1.890(46)	C(322)-C(331)	0.870(43)
C(331)-C(332)	1.664(53)	C(331)-C(341)	1.831(56)
C(331)-C(342)	1.554(50)	C(332)-C(341)	1.429(60)
C(332)-C(342)	0.942(55)	C(341)-C(342)	0.554(57)
C(35)-C(35A)	1.980	C(41)-C(42)	1.527(18)
C(43)-C(44)	1.538(19)		

ANISOTROPIC TEMPERATURE FACTORS (A X10)

ATOM	U	U	U	U	U	U
TI(1)	49(1)	43(1)	58(1)	10(1)	5(1)	1(1)
TI(2)	68(1)	42(1)	54(1)	-1(1)	2(1)	1(1)
CL(11)	56(2)	72(2)	76(2)	19(2)	1(2)	2(2)
CL(12)	74(2)	76(2)	85(2)	29(2)	24(2)	1(2)
CL(21)	143(3)	82(3)	123(3)	6(2)	-65(3)	-34(3)
CL(22)	188(4)	76(3)	101(3)	-3(2)	71(3)	24(3)
O(1)	67(5)	62(5)	56(5)	1(4)	-4(4)	-5(4)
O(2)	65(5)	41(4)	58(5)	6(4)	7(4)	1(4)
O(3)	70(5)	40(4)	74(5)	6(4)	15(4)	7(4)
O(4)	60(5)	44(4)	83(5)	-3(4)	-7(4)	5(4)
O(5)	62(5)	46(4)	81(5)	2(4)	-0(4)	3(4)
O(6)	77(5)	43(4)	88(6)	-1(4)	-1(4)	11(4)
O(8)	92(6)	37(4)	85(6)	-2(4)	-0(5)	6(4)
O(9)	110(7)	64(5)	77(6)	12(5)	11(5)	21(5)
C(11)	28(6)	43(7)	63(7)	16(6)	-6(5)	-1(5)
C(12)	32(6)	45(6)	59(7)	13(6)	2(5)	-2(5)
C(13)	44(7)	59(7)	77(8)	-6(6)	-3(6)	1(6)
C(14)	73(8)	58(7)	72(8)	18(6)	-24(6)	0(7)
C(15)	84(9)	89(9)	41(7)	11(6)	9(6)	4(7)

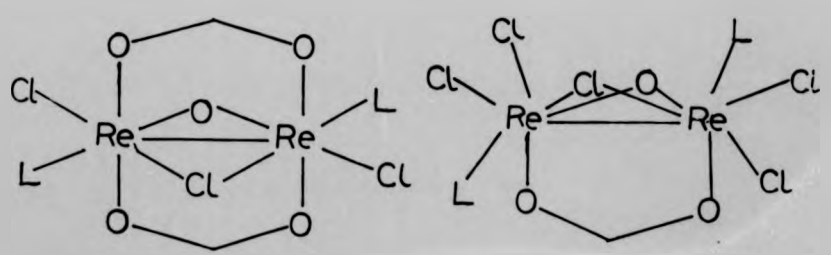
BOND ANGLES (DEG.)

CL(11)-TI(1)-CL(12)	94.8(1)	CL(11)-TI(1)-O(1)	96.5(2)
CL(12)-TI(1)-O(1)	97.4(2)	CL(11)-TI(1)-O(2)	91.5(2)
CL(12)-TI(1)-O(2)	169.6(2)	O(1)-TI(1)-O(2)	90.0(3)
CL(11)-TI(1)-O(4)	172.0(2)	CL(12)-TI(1)-O(4)	88.8(2)
O(1)-TI(1)-O(4)	90.0(3)	O(2)-TI(1)-O(4)	84.0(3)
CL(11)-TI(1)-O(6)	89.5(2)	CL(12)-TI(1)-O(6)	89.9(2)
O(1)-TI(1)-O(6)	170.0(3)	O(2)-TI(1)-O(6)	81.9(3)
O(4)-TI(1)-O(6)	83.3(3)	CL(21)-TI(2)-CL(22)	96.4(2)
CL(21)-TI(2)-O(1)	99.0(2)	CL(22)-TI(2)-O(1)	96.4(2)
CL(21)-TI(2)-O(3)	90.0(2)	CL(22)-TI(2)-O(3)	169.7(2)
O(1)-TI(2)-O(3)	90.5(3)	CL(21)-TI(2)-O(5)	169.4(2)
CL(22)-TI(2)-O(5)	88.6(2)	O(1)-TI(2)-O(5)	89.6(3)
O(3)-TI(2)-O(5)	83.7(3)	CL(21)-TI(2)-O(8)	90.7(2)
CL(22)-TI(2)-O(8)	89.6(2)	O(1)-TI(2)-O(8)	167.9(3)
O(3)-TI(2)-O(8)	82.3(3)	O(5)-TI(2)-O(8)	80.0(3)
TI(1)-O(1)-TI(2)	137.2(4)	TI(1)-O(2)-C(11)	135.3(6)
TI(2)-O(3)-C(11)	132.0(7)	TI(1)-O(4)-C(21)	131.2(6)
TI(2)-O(5)-C(21)	134.4(6)	TI(1)-O(6)-C(322)	158.8(16)
TI(1)-O(6)-C(331)	161.2(14)	C(322)-O(6)-C(331)	36.1(20)
C(311)-O(7)-C(321)	150.7(27)	C(311)-O(7)-C(322)	75.2(16)
C(321)-O(7)-C(322)	81.8(28)	C(311)-O(7)-C(331)	117.0(20)
C(321)-O(7)-C(331)	45.2(27)	C(322)-O(7)-C(331)	42.1(20)
TI(2)-O(8)-C(41)	148.9(8)	C(41)-O(9)-C(43)	118.3(9)
O(2)-C(11)-O(3)	123.2(9)	O(2)-C(11)-C(12)	117.0(9)
O(3)-C(11)-C(12)	119.8(9)	C(11)-C(12)-C(13)	119.3(9)
C(11)-C(12)-C(17)	120.7(9)	C(13)-C(12)-C(17)	119.9(10)
C(12)-C(13)-C(14)	119.4(10)	C(13)-C(14)-C(15)	120.7(10)
C(14)-C(15)-C(16)	120.5(10)	C(15)-C(16)-C(17)	120.0(10)
C(12)-C(17)-C(16)	119.6(10)	O(4)-C(21)-O(5)	123.4(9)
O(4)-C(21)-C(22)	118.7(9)	O(5)-C(21)-C(22)	117.9(9)
C(21)-C(22)-C(23)	121.2(9)	C(21)-C(22)-C(27)	121.1(9)
C(23)-C(22)-C(27)	117.5(9)	C(22)-C(23)-C(24)	121.6(10)
C(23)-C(24)-C(25)	119.0(12)	C(24)-C(25)-C(26)	121.9(11)
C(25)-C(26)-C(27)	117.8(12)	C(22)-C(27)-C(26)	122.2(11)
O(7)-C(311)-C(322)	44.1(12)	O(7)-C(311)-C(35)	87.6(11)
C(322)-C(311)-C(35)	130.7(14)	O(7)-C(321)-C(322)	66.6(26)
O(7)-C(321)-C(331)	99.3(38)	C(322)-C(321)-C(331)	40.3(27)
O(7)-C(321)-C(332)	170.5(35)	C(322)-C(321)-C(332)	104.1(24)
C(331)-C(321)-C(332)	71.3(31)	O(7)-C(321)-C(342)	144.6(32)
C(322)-C(321)-C(342)	94.2(21)	C(331)-C(321)-C(342)	54.3(28)
C(332)-C(321)-C(342)	29.8(18)	O(6)-C(322)-O(7)	166.4(29)
O(6)-C(322)-C(311)	132.5(25)	O(7)-C(322)-C(311)	60.6(15)
O(6)-C(322)-C(321)	136.3(27)	O(7)-C(322)-C(321)	31.7(15)
C(311)-C(322)-C(321)	91.0(20)	O(6)-C(322)-C(331)	99.6(33)
O(7)-C(322)-C(331)	66.9(30)	C(311)-C(322)-C(331)	127.1(35)
C(321)-C(322)-C(331)	39.7(28)	O(6)-C(331)-O(7)	115.4(26)
O(6)-C(331)-C(321)	140.9(36)	O(7)-C(331)-C(321)	35.5(23)
O(6)-C(331)-C(322)	44.3(24)	O(7)-C(331)-C(322)	71.0(31)
C(321)-C(331)-C(322)	100.0(43)	O(6)-C(331)-C(332)	118.0(25)
O(7)-C(331)-C(332)	114.9(28)	C(321)-C(331)-C(332)	79.4(32)
C(322)-C(331)-C(332)	143.6(37)	O(6)-C(331)-C(341)	119.4(25)
O(7)-C(331)-C(341)	123.0(28)	C(321)-C(331)-C(341)	98.5(34)
C(322)-C(331)-C(341)	160.1(40)	C(332)-C(331)-C(341)	48.0(22)
O(6)-C(331)-C(342)	114.6(25)	O(7)-C(331)-C(342)	130.1(29)
C(321)-C(331)-C(342)	99.1(34)	C(322)-C(331)-C(342)	158.8(39)
C(332)-C(331)-C(342)	33.8(21)	C(341)-C(331)-C(342)	16.4(20)
C(321)-C(332)-C(331)	29.3(16)	C(321)-C(332)-C(341)	84.6(29)
C(331)-C(332)-C(341)	72.1(29)	C(321)-C(332)-C(342)	84.8(37)
C(331)-C(332)-C(342)	66.7(35)	C(341)-C(332)-C(342)	13.1(31)
C(331)-C(341)-C(332)	59.9(26)	C(331)-C(341)-C(342)	52.2(58)
O(7)-C(322)-C(331)	66.9(30)	C(311)-C(322)-C(331)	127.1(35)
C(321)-C(322)-C(331)	39.7(28)	O(6)-C(331)-O(7)	115.4(26)
O(6)-C(331)-C(321)	140.9(36)	O(7)-C(331)-C(321)	35.5(23)
O(6)-C(331)-C(322)	44.3(24)	O(7)-C(331)-C(322)	71.0(31)
C(321)-C(331)-C(322)	100.0(43)	O(6)-C(331)-C(332)	118.0(25)
O(7)-C(331)-C(332)	114.9(28)	C(321)-C(331)-C(332)	79.4(32)
C(322)-C(331)-C(332)	143.6(37)	O(6)-C(331)-C(341)	119.4(25)
O(7)-C(331)-C(341)	123.0(28)	C(321)-C(331)-C(341)	98.5(34)
C(322)-C(331)-C(341)	160.1(40)	C(332)-C(331)-C(341)	48.0(22)
O(6)-C(331)-C(342)	114.6(25)	O(7)-C(331)-C(342)	130.1(29)
C(321)-C(331)-C(342)	99.1(34)	C(322)-C(331)-C(342)	158.8(39)
C(332)-C(331)-C(342)	33.8(21)	C(341)-C(331)-C(342)	16.4(20)
C(321)-C(332)-C(331)	29.3(16)	C(321)-C(332)-C(341)	84.6(29)
C(331)-C(332)-C(341)	72.1(29)	C(321)-C(332)-C(342)	84.8(37)
C(331)-C(332)-C(342)	66.7(35)	C(341)-C(332)-C(342)	13.1(31)
C(331)-C(341)-C(332)	59.9(26)	C(331)-C(341)-C(342)	52.2(58)
C(332)-C(341)-C(342)	22.6(54)	C(321)-C(342)-C(331)	26.7(16)
C(321)-C(342)-C(332)	65.5(34)	C(331)-C(342)-C(332)	79.5(37)
C(321)-C(342)-C(341)	108.8(67)	C(331)-C(342)-C(341)	111.5(68)
C(332)-C(342)-C(341)	144.3(81)	C(311)-C(35)-C(35A)	150.8(4)
O(8)-C(41)-O(9)	119.3(12)	O(8)-C(41)-C(42)	126.2(11)
O(9)-C(41)-C(42)	114.4(10)	O(9)-C(43)-C(44)	103.3(10)

the carboxylate groups. Thus the molecule is symmetrical about the plane containing the μ-oxygen, and the two titanium atoms. This is the greatest deviation from a perfect octahedral geometry, but as a consequence of this other angles deviate from those found in the perfect octahedron.

It is interesting to note that a related structural type has been identified previously in an osmium (IV) derivative, $Os_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2Cl_4(PPh_3)_2$[175]. This compound, prepared by the reaction of $Os_2O_2Cl_4(PPh_3)_2$ and acetic acid, has an isomeric structure to (III) and (IV) in which a chlorine atom, rather than the ligand molecule, is *trans* to the μ-oxo atom. The molecular dimensions of this compound are very similar to those of (III) and (IV).

Other bridged systems such as $Re_2(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}O_2CC_2H_5)_2Cl_2(PPh_3)_2$[176] and $Re_2(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-}O_2CC_2H_5)Cl_4(PPh_3)_2$[177] are more distantly related, but like many bimetallic carboxylates these compounds contain metal-metal bonds.



Traces of the hydrolysis product were observed in EtOAc solution, even after attempts to rigorously dry the solvent. It was noticed, however, that the solubility of the mono-carboxylates in EtOAc increased markedly on addition of traces of water. With THF which could be completely dried by distillation from sodium-benzophenone ketal, the compounds $TiCl_3(O_2CR)$ were insoluble at room temperature, but did dissolve on heating. On cooling solids precipitated, which when isolated were essentially unchanged but were shown to contain unco-ordinated THF as resonances were observed at 2.05 and 4.40 p.p.m. in the ^1H n.m.r. spectrum of the solid when dissolved in $CDCl_3$ solution.

An alternative approach to the preparation of adducts of the compounds $TiCl_3(O_2CR)$ is the reaction of the appropriate carboxylic acid with the THF adduct of $TiCl_4$, $TiCl_4 \cdot 2THF$ in benzene solution. However, when both the acid and the solvent are rigorously dry the solvated forms of $TiCl_3(O_2CR)$ described above precipitates from the reaction mixtures.

$$TiCl_4 \cdot 2THF + RCO_2H \rightarrow TiCl_3(O_2CR) \cdot nTHF + HCl$$

When half a mole equivalent of water is added to a solution of $TiCl_4 \cdot 2THF$ and a carboxylic acid in benzene, the oxygen bridged compounds $[TiCl_2(O_2CR) \cdot THF]_2O$ precipitate from solution in high yield. When isolated these compounds were identified by comparison of their i.r. and ^1H n.m.r. spectra with those of authentic samples.

3.9. Infra-Red Spectra of the Oxo-Bridged Compounds

The bands in the i.r. spectra of the EtOAc and THF adducts of the oxo-bridged dimers, $[TiCl_2(O_2CR)L]_2O$, in the carboxylate stretching region are shown in the Table below (those due to other absorptions are omitted).

$\nu(CO_2)$ (cm^{-1})				R	L
1665		1540	1410	Me	EtOAc
		1550	1410	Me	THF
1665		1520	1420	CMe_3	EtOAc
		1525	1420	CMe_3	THF
1650	1600	1520	1410	Ph	EtOAC
	1600	1520	1410	Ph	THF

When half a mole equivalent of water is added to a solution of $TiCl_4 \cdot 2THF$ and a carboxylic acid in benzene, the oxygen bridged compounds $[TiCl_2(O_2CR) \cdot THF]_2O$ precipitate from solution in high yield. When isolated these compounds were identified by comparison of their i.r. and ^1H n.m.r. spectra with those of authentic samples.

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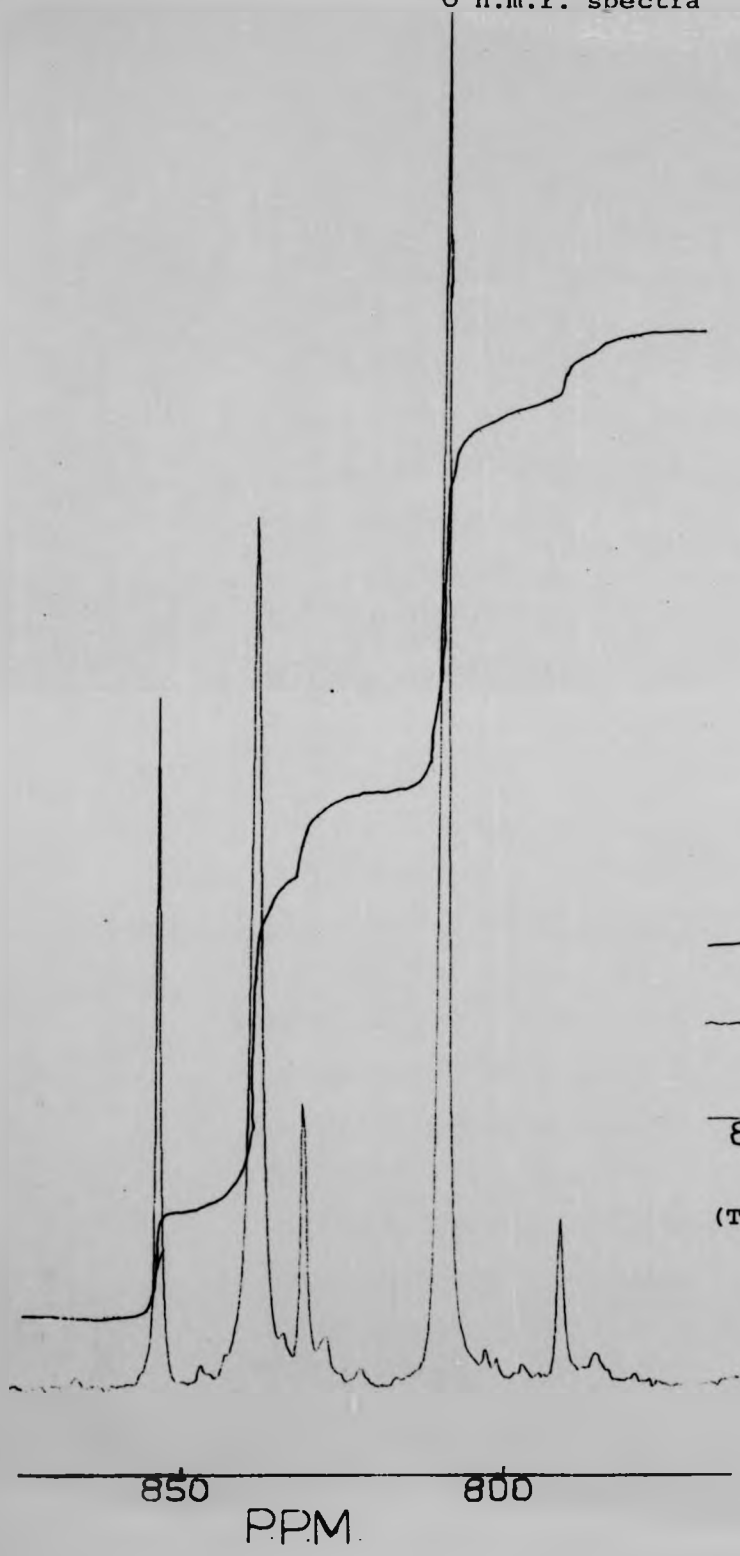
1665		1540	1410	Me	EtOAc
		1550	1410	Me	THF
1665		1520	1420	CMe_3	EtOAc
		1525	1420	CMe_3	THF
1650	1600	1520	1410	Ph	EtOAC
	1600	1520	1410	Ph	THF

The bands near 1650 cm^{-1} in the spectra of the EtOAc adducts are assigned to the carbonyl stretch of the co-ordinated ligand, which is consistent with the lowering of the stretching frequency (128 cm^{-1}) observed when EtOAc is co-ordinated to Ti(IV) in $(TiCl_4 \cdot EtOAc)_2$[112]. The bands at 1600 cm^{-1} observed in the spectra of the benzoate complexes are assigned to a phenyl ring stretch, as they are only observed in these spectra.

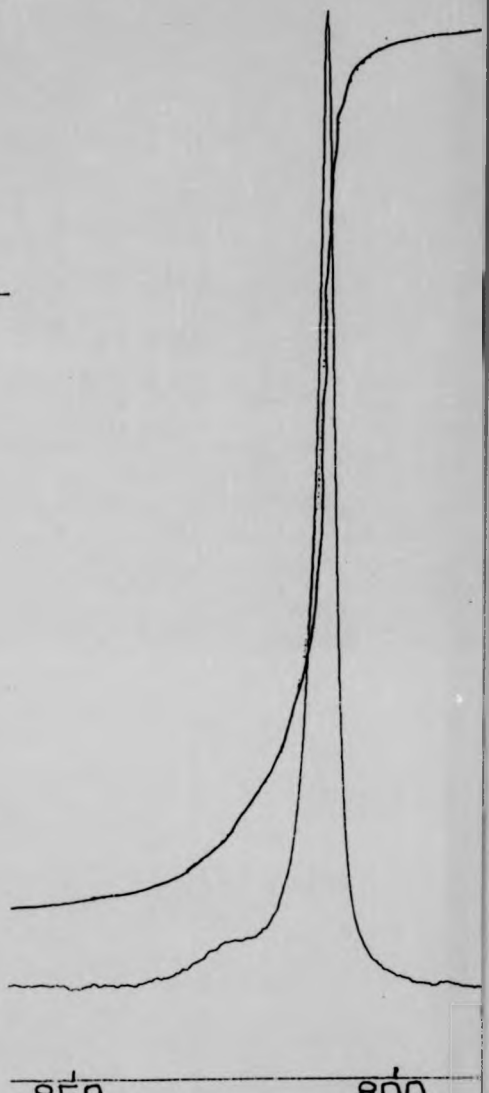
Therefore there are only two other bands in this region of these spectra, one at 1550-1520 cm^{-1}, which is assigned at $\nu(CO_2)_{asym}$, and one at 1420-1410 cm^{-1}, which is assigned as $\nu(CO_2)_{sym}$. The average value of Δ for these compounds is therefore approximately 100 cm^{-1}, which compares with values of 180-150 cm^{-1} found in cyclopentadienyl compounds. However, these compounds contained Ti(III), and so the comparison will not be entirely valid.

The values of Δ for bridging carboxylates vary depending on the metal, but are generally close to 150 cm^{-1} though values less than 100 cm^{-1} have been reported[135].

^{17}O n.m.r. spectra



$TiCl_3(O_2CPh) + H_2O$ in THF



$(TiCl_2(O_2CPh)\cdot THF]_2O$

3.10. ^{17}Oxygen Labelling Experiments

The oxo-bridge in the compound $(TiCl_2(O_2CPh)THF)_2O$ was shown to arise from the water used for the hydrolysis, and not for example by degradation of the carboxylate group, by ^{17}O labelling experiments. When half a mole equivalent of $H_2{}^{17}O$ is added to a suspension of $TiCl_3(O_2CPh)$ in THF, the solid dissolves immediately to give a red solution. The ^{17}O n.m.r. spectrum of this solution shows several signals in the 750-850 p.p.m. region (relative to $H_2{}^{17}O$ = 0), where signals corresponding to oxygen bonded to titanium would be expected[178]. On standing yellow crystals form in the solution. The crystals, after removal of supernatant, washing with petroleum ether, and drying in *vacuo* were identified as $[TiCl_2(O_2CPh)\cdot THF]_2O$ by comparison of their ^1H n.m.r. and i.r. spectra with those of an authentic sample. When these crystals are dissolved in $CDCl_3$, the ^{17}O n.m.r. spectrum shows a single resonance at 810 p.p.m., which had been observed as the major signal among the other signals in the spectrum of the original reaction mixture. This shows that the oxygen bridge in (III) arises directly from the added water, and that (III) can be prepared in high yield in a controlled manner.

Further experiments show that (III) is the major product when labelled water is added to $TiCl_3(O_2CPh)$ in THF in a series of molar ratios up to 1:2; H_2O:Ti. In the ^{17}O n.m.r. spectra, the resonance at 810 p.p.m. was always the most intense, but other resonances at 834, 841 and 857 p.p.m. were always prominent. On addition of more water these signals grow in intensity. These signals obviously arise from other hydrolysis products, as yet unidentified, in the reaction mixture. Such species could form when the local concentration of water in the reaction mixture is high, or when more than half a mole equivalent of water is added.

The spectra do not change over a period of 2 weeks, and it is therefore unlikely that the signals are due to intermediates in the formation of (III).

Further Hydrolysis

As described above the ^{17}O n.m.r. spectra of THF solutions of $TiCl_3(O_2CPh)$ with added labelled water are complicated. When water was added to (III) in THF solution no precipitation occurred, but a white solid was produced when the pale yellow clear solution was pumped to dryness. Elemental analysis showed this to be inhomogeneous. Neither the i.r. nor the ^1H n.m.r. spectra of this

solid were well resolved. A set of resonances in the region 7.0 - 8.0 p.p.m. in the ^1H n.m.r. spectrum indicated that the solid contained some benzoate groups, but the only distinguishable features of the i.r. spectrum were broad bands centred at 3500 and 1600 cm^{-1} due to water.

3.11. Reaction of the Compounds $TiCl_3(O_2CR)$ with Methanol

When one mole equivalent of methanol, which was dried by distillation from magnesium metal, and then from calcium hydride, was added dropwise to warm solutions of compounds of the type $TiCl_3(O_2CR)$ in THF, yellow crystals formed in the solution over about one week. These were isolated by removal of the supernatant, washing with petroleum ether, and drying in *vacuo*. Comparison of the i.r. and ^1H n.m.r. spectra of these crystals show that they were all the same compound. Analytical data confirmed that in the reaction of the mono-carboxylates with methanol the titanium carboxylate bond is broken and the compound $TiCl_3(OMe)\cdot 2THF$ was formed.

$$TiCl_3(O_2CR) + MeOH \xrightarrow{THF} TiCl_3(OMe)\cdot 2THF + RCO_2H$$

The i.r. spectra of the products show no bands

which can be assigned to carboxylate stretches. The ^1H n.m.r. spectra show singlets at 2.05 and 4.35 p.p.m. which are assigned to THF protons, and a singlet at 4.85 p.p.m. which is consistent with the protons of a methoxide group, but no signals which could be assigned to a carboxylate group were observed.

When $TiCl_3(O_2CPh)$ in THF was treated with methanol that had not been dried then yellow crystals which were subsequently identified as (III), precipitated from solution.

3.12. Other Adducts of $[TiCl_2(O_2CR)]_2O$

The EtOAc adducts of compounds of the type $[TiCl_2(O_2CR)]_2O$ were found to be stable indefinitely in a nitrogen atmosphere. However, the THF adducts decomposed slowly, both in the solid phase and in solution, to give inhomogeneous green products which probably arise from reduction of Ti(IV) to Ti(III) by cleavage of THF.

Attempts to prepare other adducts of the oxo bridged dimer were unsuccessful because reduction of titanium occurred in each case. The ligand EtOAc was displaced from (IV) in benzene solution by molar equivalents of pyridine, acetonitrile,

triphenyl phosphine, and triethyl phosphine, and yellow precipitates were formed. After recovery and drying, all these adducts darken to inhomogeneous green solids. The rate of this decomposition varied with the ligand. It was apparent within one hour of the preparation of the pyridine adduct, and after four hours in the case of both phosphine adducts. The aceto-nitrile adduct is more stable, but it also turned green over a few days.

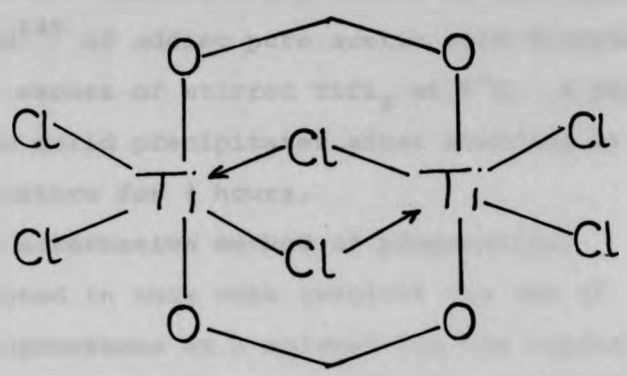
As a consequence of this reduction the analyses of these adducts are inconsistent, but indicated that the expected adducts did form initially.

3.13. The Structure of Compounds of the Type $TiCl_3(O_2CR)$

The observations reported above suggest that compounds of the type $TiCl_3(O_2CR)$ possess a dimeric structure, and this is supported by the measured molecular weight of $TiCl_3(O_2CCMe_3)$, 430 which is close to that of a dimer, 510.

Compounds (III) and (IV) are shown to have dimeric structures by X-ray methods, and it is unlikely that dimerization takes place on hydrolysis. Therefore assuming that the titanium atoms are six co-ordinate in these compounds, and that there is a double carboxylate bridge, as in

(III) and (IV), then the structure shown below is proposed for the compounds $TiCl_3(O_2CR)$.



This structure is consistent with evidence from the i.r. spectra of these compounds. The oxo-bridged compounds are good models for this system. As discussed in Section 3.9 values of 140, 110 and 95 cm^{-1} for Δ were assigned for the acetate, benzoate and trimethyl acetate respectively. These values are within the range of Δ (190 - 50 cm^{-1}) proposed for the mono-carboxylates, discussed in Section 3.7.

It is reasonable that simple adducts of these compounds do not form if this proposed structure is correct as titanium rarely has a co-ordination number of greater than six.

3.14. Preparation of the Compounds $TiCl_2(O_2CR)_2$

The bis-acetate was prepared by the reported method[149] of adding pure acetic acid dropwise to an excess of stirred $TiCl_4$ at 0^oC. A pale yellow solid precipitates after standing at room temperature for 4 hours.

An alternative method of preparation, attempted in this work involves the use of dichloromethane as a solvent for the reaction. Acetic acid and $TiCl_4$ were mixed in a stoicheiometric ratio for the formation of $TiCl_2(O_2CMe)_2$ ($MeCO_2H:TiCl_4$ = 2:1) in dry CH_2Cl_2, and the resulting yellow solution was stirred magnetically for 2 days. A pale yellow precipitate formed gradually. The supernatant was removed, the solid washed with petroleum ether, and dried in *vacuo*.

The i.r. spectra of the solids prepared by the two different methods are identical, and analytical data established the compounds as $TiCl_2(O_2CMe)_2$.

The compound $TiCl_2(O_2CCMe_3)_2$ was prepared by adding half a mole equivalent of $TiCl_4$ to a solution of Me_3CCO_2H in toluene. The orange solution was heated to reflux for 2 hours, and a white semi-crystalline solid precipitated on standing at -20^oC overnight, and was recovered and dried in the usual way.

Both of the bis-carboxylates, $TiCl_2(O_2CR)_2$ (R = Me, CMe_3), are insoluble in benzene, toluene and chlorinated solvents.

It was not possible to prepare $TiCl_2(O_2CPh)_2$ by either direct reaction of $TiCl_4$ with $PhCO_2H$, or by reaction in CH_2Cl_2 or toluene, as the product contained unreacted benzoic acid and $TiCl_3(O_2CPh)$, even after extended times of reactions.

3.15. Infra-Red Spectra of the Bis-Carboxylates

The i.r. spectra of $TiCl_2(O_2CMe)_2$ and $TiCl_2(O_2CCMe_3)_2$ are similar in the carboxylate stretching region. In the spectrum of $TiCl_2(O_2CCMe_3)_2$ as a mull in nujol on hexafluorobutadiene four bands are observed which can be assigned to carboxylate stretches. These are at 1665, 1580, 1515 and 1410 cm^{-1}. Amaudrut[150] reported a spectrum of this compound which was very similar to that observed here, except he reported a broad band at 1520 cm^{-1} which was not resolved into two bands.

The i.r. spectrum of $TiCl_2(O_2CMe)_2$ is identical to that reported by Amaudrut[150], with bands in the carboxylate stretching region at 1655, 1550 and 1430 cm^{-1}. The band at 1550 cm^{-1}

could not be resolved into two bands, as in the case of $TiCl_2(O_2CCMe_3)_2$.

These observations are consistent with the presence of two types of carboxylates in these compounds. The probable values of Δ for the bis-trimethyl acetate compound are 150 and 170 cm^{-1}. These values are comparable to the values of 150 - 180 cm^{-1} for Δ for bridging carboxylates found in titanium cyclopentadienyl derivatives, though bidentate co-ordination cannot be ruled out (Δ = 110 cm^{-1}). Thus these observations are consistent with the structure proposed by Amaudrut *et al* for compounds of the type $TiCl_2(O_2CR)_2$ on the basis of i.r. and Raman spectra[151], as shown in Section 3.2.2.

3.16. Reactions of Compounds of the Type $TiCl_2(O_2CR)_2$

The bis-carboxylates, $TiCl_2(O_2CR)$ (R = Me, CMe_3), are insoluble in all organic solvents. However, they do dissolve in co-ordinating solvents when water is added to these solvents. Thus both $TiCl_2(O_2CMe)_2$ and $TiCl_2(O_2CCMe_3)_2$ were insoluble in dried THF, even on reflux, but both dissolved immediately on addition of half a mole equivalent of water to the respective suspensions to produce pale yellow solutions. On concentration

of the solutions by pumping, yellow crystals formed. The supernatants were removed, the crystals washed with petroleum ether, and dried in *vacuo*.

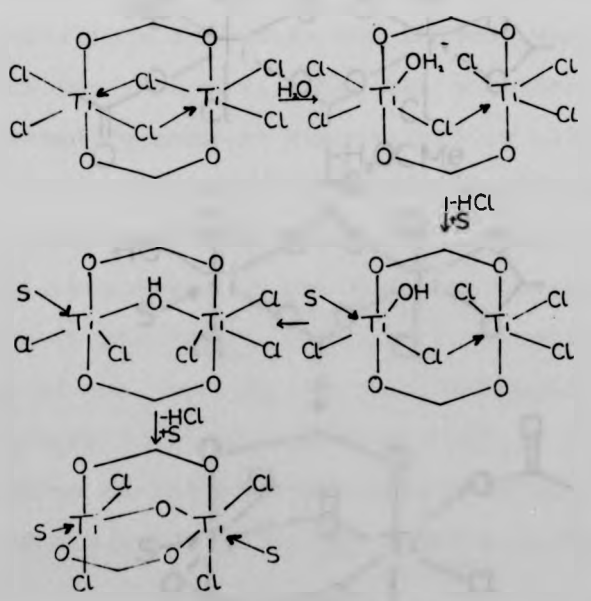
Comparison of the i.r. and ^1H n.m.r. spectra of these crystals with those of the solids produced by the controlled hydrolysis of the compounds $TiCl_3(O_2CR)$ (R = Me, CMe_3), show them to be the same compounds, $[TiCl_2(O_2CR)\cdot THF]_2O$.

The compounds $[TiCl_2(O_2CR)\cdot EtOAc]_2O$ (R = Me, CMe_3) can be similarly shown to be produced by the action of water on the appropriate carboxylates in EtOAc solution.

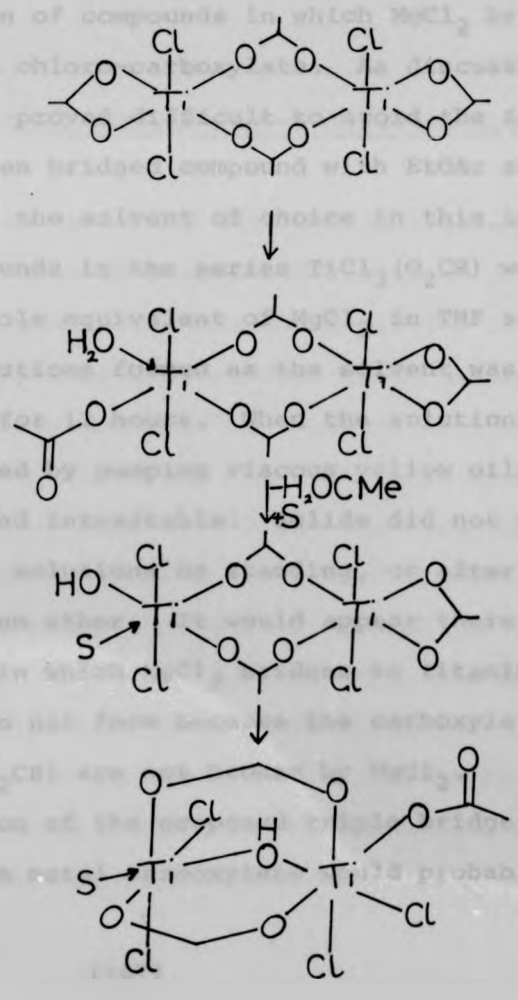
Therefore it seems that the compounds $[TiCl_2(O_2CR)L]_2O$ (R = Me, CMe_3, Ph; L = THF, EtOAc) are particularly stable intermediates in the hydrolysis reactions of titanium chloro carboxylates since they are formed in the reactions of both mono- and bis-carboxylates. In the former a Ti-Cl bond is hydrolysed, and in the latter a Ti-carboxylate is hydrolysed by water, in the co-ordinating solvents THF and EtOAc. The reason for this stability must lie in the detailed geometry of the oxygen/carboxylate triple bridge. There must also be an accessible mechanism for the formation of these compounds from both the mono- and bis-carboxylates. These hydrolysis

reactions are probably initiated by the co-ordination of a water molecule to a titanium atom. The properties of the mono- and bis carboxylates probably differ in this respect, and this could lead to the formation of the same final products in their reactions. Proposed mechanisms are described below.

Chloro-bridges are known to be labile in titanium(IV) complexes. Thus co-ordination of water to a mono-carboxylate could break a chloro-bridge, and then hydrolysis of a Ti-Cl bond occurs. Attack on the other titanium atom of the dimer follows as the oxo-bridge is formed by hydrolysis of another Ti-Cl bond. The bridging carboxylates are forced into a *cis* orientation from their original *trans* conformation.



Co-ordination of water to a bis-carboxylate is likely to take place via a bidentate carboxylate being forced to adopt a unidentate mode of co-ordination. This may make it more susceptible to hydrolysis so that a carboxylate is eliminated rather than a chloride. Subsequent attack on the other titanium atom in the dimer follows a similar sequence, and the triply bridged compound is formed.



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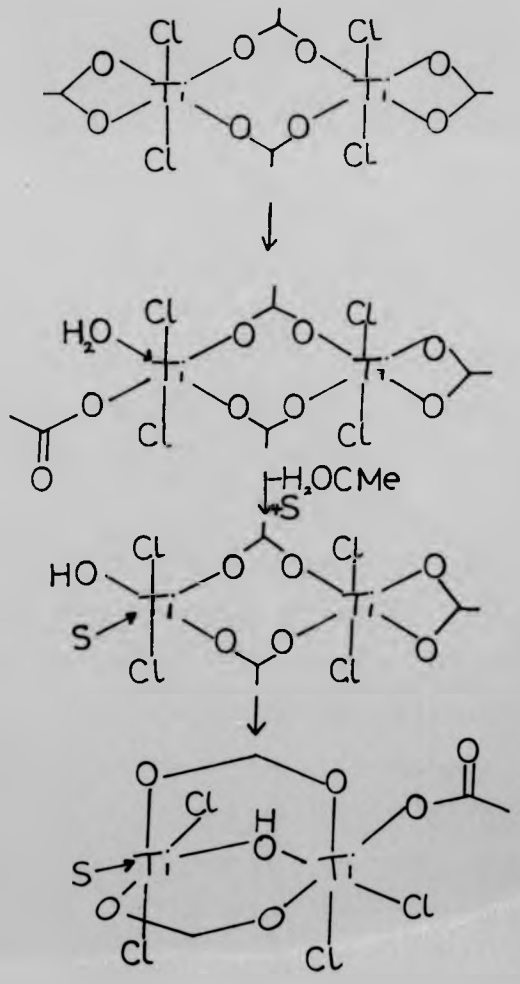


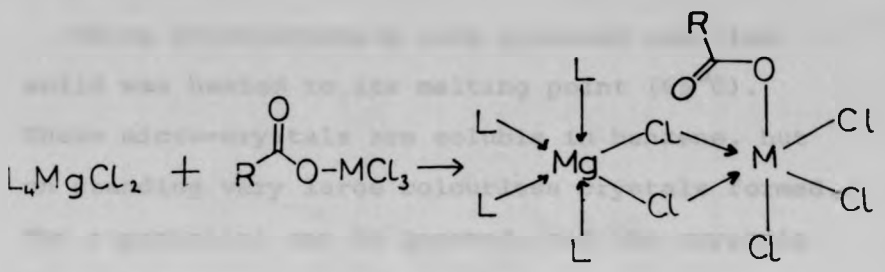
This scheme assumes that a bidentate carboxylate is more susceptible to hydrolysis than a bridging carboxylate. This is reasonable in that there is less angle strain in a carboxylate group when it is bridging rather than chelating.

3.17. Reactions of $TiCl_3(O_2CR)$ with $MgCl_2$ in EtOAc

The original aim of this investigation was the preparation of compounds in which $MgCl_2$ bridges to a titanium chloro-carboxylate. As discussed earlier it proved difficult to avoid the formation of an oxygen bridged compound with EtOAc as solvent, so THF was the solvent of choice in this investigation. When compounds in the series $TiCl_3(O_2CR)$ were mixed with one mole equivalent of $MgCl_2$ in THF solution yellow solutions formed as the solvent was heated to reflux for 12 hours. When the solutions were concentrated by pumping viscous yellow oils formed which proved intractable. Solids did not precipitate from these solutions on standing, or after addition of petroleum ether. It would appear therefore that compounds in which $MgCl_2$ bridges to titanium probably do not form because the carboxylate bridges in $TiCl_3(O_2CR)$ are not broken by $MgCl_2$.

Formation of the proposed triple bridge between $MgCl_2$ and a metal carboxylate would probably require

a unidentate carboxylate.

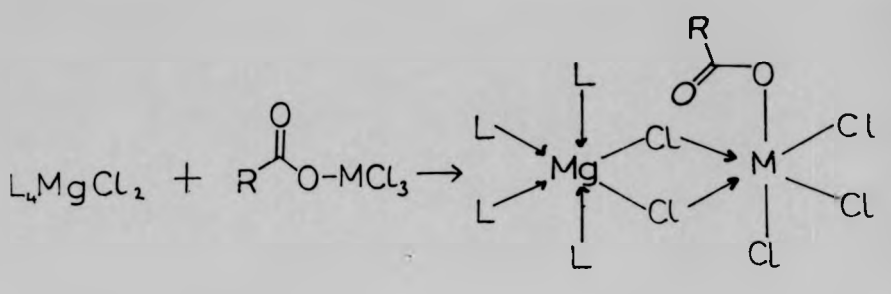


3.18. Preparation and Properties of Tin(IV) Carboxylates

As the synthesis of carboxylate-bridged magnesium-titanium dimers had failed to yield well defined compounds the analogous tin(IV) chloro mono-carboxylates were studied in an attempt to prepare a heterobimetallic compound with $MgCl_2$.

When $SnCl_4$ was added dropwise to an excess of stirred acetic acid at 0^oC and the resulting clear solution heated to 80^oC for 2 hours, a solid precipitate was not formed on cooling, or on standing at -20^oC for 2 weeks. This was also the case when equimolar amounts of $SnCl_4$ and acetic acid were mixed and heated to reflux in CH_2Cl_2, Et_2O, or benzene. When the solvents were removed by pumping a viscous oil resulted. It proved

a unidentate carboxylate.



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When $SnCl_4$ was added dropwise to an excess of stirred acetic acid at $0^{o}C$ and the resulting clear solution heated to $80^{o}C$ for 2 hours, a solid precipitate was not formed on cooling, or on standing at $-20^{o}C$ for 2 weeks. This was also the case when equimolar amounts of $SnCl_4$ and acetic acid were mixed and heated to reflux in CH_2Cl_2, Et_2O, or benzene. When the solvents were removed by pumping a viscous oil resulted. It proved

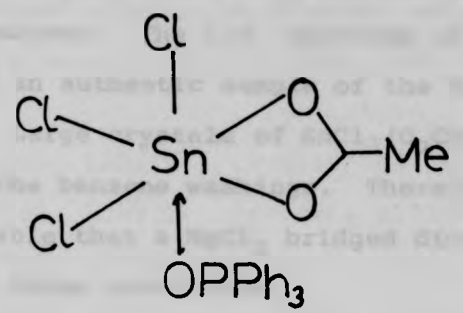
very difficult to characterise this oil, but a white solid precipitated from the EtOAc solution of the oil.

White micro-crystals were produced when the solid was heated to its melting point (65°C). These micro-crystals are soluble in benzene, but on standing very large colourless crystals formed. The supernatant can be removed, and the crystals dried in *vacuo*.

The crystals are formulated as $SnCl_3(O_2CMe)\cdot$ EtOAc on the basis of analytical data and evidence from their ^1H n.m.r. spectrum. The quartet and triplet expected for the ethyl group of EtOAc were observed at 4.32 and 1.38 p.p.m. respectively. However, two signals are observed at 2.32 and 2.42 p.p.m. in $CDCl_3$ solution. These signals are better resolved when the solid is dissolved in C_6D_6 as the singlets are observed at 1.30 and 1.70 p.p.m. In both solutions the signals are of equal intensity indicating that equal amounts of EtOAc and $CH_3CO_2^-$ are present in the solid.

The i.r. spectrum of the solid shows bands at 1690, 1615 and 1535 cm^{-1}. The band at 1690 cm^{-1} is consistent with the carbonyl stretching frequency of EtOAc co-ordinated to Sn(IV) so the other two bands may be assigned as the carboxylate stretches, giving a value of Δ = 80 cm^{-1}. This is consistent

with the carboxylate being bridging or chelating rather than unidentate. In the related monomeric compound $SnCl_3(O_2CMe)\cdot Ph_3PO$, the carboxylate chelates one metal centre which is six co-ordinate[179].



Attempts to prepare benzoates of tin(IV) failed. When equimolar amounts of $SnCl_4$ and $PhCO_2H$ were mixed in toluene, and the resulting clear solution was refluxed for 2 hours, white crystals precipitated on cooling to room temperature. The i.r. spectrum of these crystals, recovered and dried as usual showed that they are the previously reported adduct $SnCl_4\cdot PhCO_2H$[153].

When equimolar amounts of $SnCl_4$ and $PhCO_2H$ were mixed in THF or EtOAc, and the resulting solutions were refluxed for 2 hours white crystals precipitated on standing for about one week. The solids isolated from the two solvents were shown to be identical. The i.r. spectrum of this solid showed it to be unreacted benzoic acid.

As with the titanium analogue the reaction of

$SnCl_3(O_2CMe)\cdot EtOAc$ with an equimolar amount of $MgCl_2$ in EtOAc produced a viscous oil after the bulk of the solvent had been removed by pumping. When this oil was washed with benzene a white residue remained. The i.r. spectrum is identical to that of an authentic sample of the EtOAc solvate of $MgCl_2$. Large crystals of $SnCl_3(O_2CMe)\cdot EtOAc$ formed in the benzene washings. Therefore it seems probable that a $MgCl_2$ bridged dimer does not form under these conditions.

3.19. Experimental

Preparation of $TiCl_3(O_2CMe)$

Method (i)

Acetic acid (1.50 cm^3, 23.8 mmol) was added dropwise to magnetically stirred $TiCl_4$ (10.0 cm^3, 91.2 mmol) at 0°C. Fumes of HCl were evolved from the resulting red solution as a yellow solid precipitated. The supernatant was removed, the solid was washed with CCl_4 (2 x 50 cm^3), and then petroleum ether (2 x 50 cm^3), and then dried in *vacuo* for 3 hours. (Yield 4.42g, 87%).

Method (ii)

Acetic acid (1.50 cm^3, 23.8 mmol) was added dropwise to a magnetically stirred solution of

$TiCl_4$ (10.0 cm^3, 91.2 mmol) in dichloromethane (30 cm^3). A yellow precipitate formed in the red solution on stirring for 16 hours. The supernatant was removed, the solid was washed with petroleum ether (3 x 30 cm^3), and dried in *vacuo* for 3 hours. (Yield 3.20g, 63%).

i.r.	1655(w)	1590(s)	1540(s)	1470(s)	1445(s)
	1405(s)	1380(s)	1270(w)	1025(m)	970(w)
	915(w)	775(m)	725(m)	665(w)	640(m)
	620(m)	560(m)	400(s)	280(m)	cm^{-1}

^1H n.m.r. 1.75 (s) p.p.m.

Analysis based on $TiCl_3C_2H_3O_2$:

calculated:	Ti, 22.45;	Cl, 49.91;	C, 11.25;	H, 1.41%
found:	22.63	50.23	11.01;	1.29

Preparation of $TiCl_3(O_2CCMe_3)$

$TiCl_4$ (5.0 cm^3, 4.56 mmol) was added dropwise to a magnetically stirred solution of Me_3CCO_2H (2.55g, 25.0 mmol) in toluene (30 cm^3). The resulting orange solution was heated to 100°C for 30 minutes. An orange crystalline precipitate formed on standing at -20°C. The supernatant was removed, the solid was washed with petroleum ether (3 x 30 cm^3), and dried in *vacuo* for 3 hours. (Yield 2.58g, 42%).

i.r. 1600(s) 1550(w) 1460(s) 1410(m) 1380(s)
1225(s) 1030(w) 940(w) 870(m) 780(w)
755(w) 720(w) 610(s) 560(w) 470(w)
430(s) 410(s) 370(m) 370(w) cm^{-1}

^1H n.m.r. 1.42(s) p.p.m.

Analysis based on $TiCl_3C_5H_9O_2$:

calculated: Ti, 18.75; Cl, 41.70%

found: 18.79 42.03

Preparation of $TiCl_3(O_2CPh)$

$TiCl_4$ (5.0 cm^3, 45.6 mmol) was added dropwise to a magnetically stirred solution of $PhCO_2H$ (2.44g, 20.0 mmol) in toluene (50 cm^3). A yellow precipitate formed immediately, but this dissolved to form a red solution when the suspension was heated to 110°C for 1 hour. On cooling to room temperature an orange precipitate formed. The supernatant was removed, the solid was washed with petroleum ether (10 x 30 cm^3), and dried in *vacuo* for 3 hours. (Yield 4.9g, 89%).

i.r. 1600(s) 1555(s) 1500(s) 1460(s) 1410(m)
1380(s) 1315(m) 1180(m) 1160(s) 1100(m)
1070(w) 1025(m) 1000(w) 850(w) 800(m)
750(s) 690(s) 570(m) 640(m) 620(s)
570(s) 510(s) 410(s) 375)s) 320(m)
290(w) 260(m) cm^{-1}

^1H n.m.r. 7.5-8.5 (m) p.p.m.

Analysis based on $TiCl_3C_7H_5O_2$:

calculated: Ti, 17.39; Cl, 38.67;C,30.50; H, 1.82%

found: 17.41 38.73 30.63 1.87

Preparation of $TiCl_2(O_2CMe)_2$

Method (i)

Acetic acid (10.0 cm^3, 175 mmol) was added dropwise to magnetically stirred $TiCl_4$ (5.0 cm^3, 45.6 mmol) at 0°C. A yellow precipitate formed immediately, and the mixture was then heated to 80°C for 5 minutes. The supernatant was removed, the solid was washed with diethyl ether (2 x 30 cm^3) and petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 3 hours. (Yield 7.65g, 70%).

Method (ii)

Acetic acid (10.0 cm^3, 175 mmol) was added dropwise to a magnetically stirred solution of $TiCl_4$ (5.0 cm^3, 45.6 mmol) in CH_2Cl_2 (30 cm^3). On stirring the resulting yellow solution for 2 days a pale yellow precipitate formed, and the supernatant turned pale green. The supernatant was removed, the solid was washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 3 hours. (Yield 9.0g, 83%).

i.r. 1650(S) 1545(s) 1460(s) 1430(s) 1380(s)
1240(m) 1045(m) 1025(m) 955(w) 740(s)
670(w) 650(m) 610(s) 560(s) 485(m)
410(s) 375(m) 350(m) 270(w) 250(w) cm^{-1}

Analysis based on $TiCl_2C_4H_6O_4$:

	Ti	Cl	C	H
calculated:	20.24;	29.97;	20.26;	2.55%
found:	21.03	29.13	21.13	2.67

Preparation of $TiCl_2(O_2CCMe_3)_2$

$TiCl_4$ (5.0cm^3, 45.6 mmol) was added to a magnetically stirred solution of Me_3CCO_2H (9.69g, 95.0 mmol) in toluene (30 cm^3). The resulting orange solution was heated to 100°C for 3 hours. A white crystalline solid precipitated on standing for 16 hours at -20°C. The supernatant was removed, the solid was washed with diethyl ether (30 cm^3) and petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. (Yield 10.6g, 65%).

i.r. 1665(s) 1580(s) 1515(s) 1460(s) 1410(m)
1380(s) 1280(w) 1225(s) 1200(m) 1030(w)
940(w) 910(w) 870(w) 810(w) 735(s)
600(s) 570(m) 525(m) 460(s) 380(s)
340(w) 320(w) 300(w) 230(m) cm^{-1}

Analysis based on $TiCl_2C_{10}H_{18}O_4$:

	Ti	Cl
calculated:	14.93;	22.12%
found:	14.56	21.35

Preparation of $[TiCl_2(O_2CMe)\cdot L]_2O$ (L = THF, EtOAc)

Water (0.045 cm^3, 2.50 mmol) was added dropwise using a micro-syringe to a magnetically stirred suspension of $TiCl_3(O_2CMe)$ (1.20g, 5.62 mmol) in THF (30 cm^3). The yellow solution which formed

immediately was heated to 60°C for 1 hour and then filtered through a celite pad. The volume of the solution was reduced to approximately two-thirds of its original value by pumping, and yellow crystals precipitated on standing at room temperature for 14 days. The yield was improved if the volume of the solution was reduced further, but the above procedure is the best to obtain crystals suitable for X-ray analysis. The supernatant was removed, the solid was washed with petroleum ether (2 x 50 cm^3), and dried in *vacuo* for 2 hours. (Yield 1.6g, 55%).

The EtOAc adduct was prepared by an identical procedure. This was recrystallized unchanged from EtOAC. (Yield 1.35g, 45%).

$[TiCl_2(O_2CMe)\cdot THF]_2O$

i.r. 1550(s) 1460(s) 1410(m) 1380(s) 1250(w)
1170(w) 1040(m) 1010(s) 950(m) 920(m)
875(m) 855(s) 815(s) 720(s) 670(s)
620(s) 550(w) 515(w) 420(s) 400(s)
350(s) 270(m) cm^{-1}

^1H n.m.r. 2.2(bs)(14H) 5.0(s)(8H) p.p.m.

Analysis based on $Ti_2Cl_4C_{12}H_{22}O_7$:

	Ti	Cl
calculated:	18.61;	27.58%
found:	17.83	27.92

$[TiCl_2(O_2CMe)\cdot EtOAc]_2O$

i.r.	1665(s)	1540(s)	1460(s)	1410(m)	1380(s)
	1310(s)	1280(m)	1235(m)	1170(w)	1155(w)
	1095(m)	1035(s)	955(w)	850(m)	750(s)
	660(m)	650(m)	616(m)	650(m)	560(m)
	560(m)	470(w)	415(s)	365(s)	250(m) cm^{-1}

^1H n.m.r. 1.40(t)(6H) 2.35(bs)(12H) 4.40(q)(4H) p.p.m.

Analysis based on $Ti_2Cl_4C_{12}H_{22}O_9$:

calculated:	Ti, 18.18;	Cl, 26.94;	C, 22.77;	H, 4.17%
found	18.75	27.78	23.63	4.29

Preparation $[TiCl_2(O_2CCMe_3)\cdot L]_2O$ (L = THF, EtOAc)

Water (0.063 cm^3, 3.50 mmol) was added dropwise to a magnetically stirred solution of $TiCl_3(O_2CCMe_3)$ (20g, 7.83 mmol) in THF (30 cm^3). The resulting yellow solution was heated to 60°C for 30 minutes and then filtered through a celite pad. The volume of the solution was reduced by approximately one half by pumping, and a yellow powder precipitated on standing at room temperature for 4 hours. The supernatant was removed, the solid was washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 3 hours. (Yield 1.46g, 30%).

The EtOAc adduct was prepared by an identical procedure. (Yield 2.1g, 42%).

$[TiCl_2(O_2CCMe_3)\cdot THF]_2O$

i.r. 1525(s) 1460(s) 1420(m) 1375(s) 1300(w)
1225(s) 1170(w) 1070(w) 1030(w) 1000(m)
920(m) 855(s) 780(w) 720(s) 680(m)
600(m) 550(w) 455(s) 390(s) 350(s)
240(m) cm^{-1}

^1H n.m.r. 1.30(t)(18H) 2.20(s)(8H) 5.00(s)(8H)p.p.m.

Analysis based on $Ti_2Cl_4C_{18}H_{34}O_7$:

calculated: Ti, 15.46; Cl, 22.91;

found: 15.39 23.32

$[TiCl_2(O_2CCMe_3)\cdot EtOAc]_2O$

i.r. 1665(s) 1520(s) 1460(s) 1420(m) 1375(s)
1310(s) 1220(s) 1040(m) 1010(s) 855(w)
720(s) 600(m) 455(s) 390(s) 350(s)
260(w) 235(w) cm^{-1}

^1H n.m.r. 1.32(m)(24H) 2.32(s)(6H) 4.34(q)(4H)p.p.m.

Analysis based on $Ti_2Cl_4C_{18}H_{34}O_9$:

calculated: Ti, 15.16; Cl, 22.47%

found: 14.97 21.89

Preparation of $[TiCl_2(O_2CPh)\cdot L]_2O$ (L = THF, EtOAc)

Water (0.054 cm^3, 3.00 mmol) was added dropwise to a magnetically stirred suspension of $TiCl_3(O_2CPh)$

(1.70g, 6.17 mmol) in THF (30 cm^3). A yellow solution was formed immediately which was heated to 60°C for 30 minutes, and then filtered through a celite pad. On standing at room temperature for two weeks a small amount of crystalline material precipitated. The yield was increased if the volume of the solution was reduced by pumping. The supernatant was removed, the solid was washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. On standing for a month under nitrogen the yellow crystals turned green.

The EtOAc adduct was prepared by an identical procedure, though in this case the solid remained yellow on standing.

$[TiCl_2(O_2CPh)\cdot THF]_2O$

i.r.	1600(m)	1530(s)	1460(s)	1410(s)	1380(s)
	1340(m)	1245(m)	1175(m)	1070(w)	1040(m)
	995(s)	920(s)	825(s)	720(s)	670(m)
	490(m)	380(s)	300(m)	240(w)	cm^{-1}

^1H n.m.r. 2.22(s)(8H) 5.00(s)(8H) 7.5-8.2(m)(10H)p.p.

Analysis based on $Ti_2Cl_4C_{22}H_{26}O_7$:

calculated:	Ti, 14.97;	Cl, 22.19%
found:	14.83	23.05

$[TiCl_2(O_2CPh)EtOAc]_2O$

i.r.	1650(s)	1600(m)	1520(s)	1460(s)	1410(s)
	1380(s)	1320(s)	1180(m)	1160(w)	1150(w)
	1100(w)	1070(w)	1040(m)	1025(m)	1010(w)
	850(m)	720(s)	625(m)	680(m)	670(m)
	610(w)	510(m)	485(s)	385(s)	350(s)
	320(m)	260(w)	230(m)	cm^{-1}	

^1H n.m.r. 1.36(t)(6H) 2.35(s)(6H) 4.38(q)(4H)
7.2-8.5(m)(10H) p.p.m.

Analysis based on $Ti_2Cl_4C_{22}H_{26}O_9$:

calculated:	Ti, 14.69;	Cl, 21.78;	C, 40.19;	H, 3.99%
found:	14.75	22.50	41.03	3.83

Reaction of $TiCl_2(O_2CMe)_2$ with H_2O in THF

Water (0.090 cm^3, 5.00 mmol) was added to a magnetically stirred suspension of $TiCl_2(O_2CMe)_2$ (2.40g, 10.4 mmol) in THF (50 cm^3). The solid dissolved immediately to give a pale yellow solution which was heated to 60°C for 30 minutes, and then filtered through a celite pad. A yellow solid precipitated when the volume of the solution was reduced by pumping. The supernatant was removed, the solid was washed with petroleum ether (3 x 30 cm^3), and dried in *vacuo* for 3 hours. The product was identified as $[TiCl_2(O_2CMe)THF]_2O$ by comparison

of its i.r. and ^1H n.m.r. spectra with that of an authentic sample. (Yield 4.35g, 85%).

When an identical procedure was followed with EtOAc as the solvent $[TiCl_2(O_2CPh)EtOAc]_2O$ was obtained.

Reaction of $TiCl_2(O_2CCMe_3)_2$ with H_2O in THF

Water (0.045 cm^3, 2.50 mmol) was added to a magnetically stirred suspension of $TiCl_2(O_2CCMe_3)_2$ (1.80g, 5.61 mmol) in THF (30 cm^3). A yellow solution formed immediately which was heated to 60°C for 30 minutes, and then filtered through a celite pad. Yellow crystals formed in this solution on standing at -20°C for 3 days. The supernatant was removed, the solid was washed with petroleum ether (3 x 30 cm^3), and dried in *vacuo* for 3 hours. The solid was identified as $[TiCl_2(O_2CCMe_3)THF]_2O$ by comparison of its i.r. and ^1H n.m.r. spectra with those of an authentic sample. (Yield 1.7g, 47%).

Reactions of $TiCl_4(THF)_2$ with $MeCO_2H$ and $PhCO_2H$

The THF adduct of $TiCl_4$, $TiCl_4 \cdot 2THF$ was prepared by adding THF (2.63g, 36.5 mmol) dropwise to a magnetically stirred solution of $TiCl_4$ (2.0 cm^3, 18.2 mmol) in petroleum ether (50 cm^3).

The yellow product precipitated immediately, the supernatant was removed, the solid was washed with petroleum ether (3 x 30 cm^3), and dried in *vacuo* for 2 hours. (Yield 4.04g, 95%).

Acetic acid (0.63 cm^3, 11.0 mmol) was added dropwise to a magnetically stirred solution of $TiCl_4 \cdot 2THF$ (2.60g, 11.1 mmol) in benzene (50 cm^3). The solution was heated to reflux temperature for 1 hour. The volume of the solution was reduced by pumping, and a yellow solid precipitated. The supernatant was removed, the solid was washed with petroleum ether (3 x 30 cm^3), and dried in *vacuo* for 2 hours. The ^1H n.m.r. spectrum of a solution of the solid in $CDCl_3$ showed that both acetate and THF were present in a ratio which was close to 1:2, but the signals corresponding to THF were at 2.05 and 4.40 p.p.m., indicating that the THF was not co-ordinated to titanium. The solid is therefore formulated as a weakly solvated form of $TiCl_3(O_2CMe)$, namely $TiCl_3(O_2CMe) \cdot 2THF$.

Similarly the reaction between $TiCl_4 \cdot 2THF$ and $PhCO_2H$ produced an impure solvated form of $TiCl_3(O_2CPh)$.

Reaction of $TiCl_3(O_2CMe)$ with MeOH in THF

Methanol (0.56 cm^3, 14.0 mmol) was added dropwise to a solution of $TiCl_3(O_2CMe)$ (3.0g, 14.1 mmol) in THF (30 cm^3). The resulting yellow solution was filtered through a celite pad. On standing for 2 days yellow crystals formed in the solution. The supernatant was removed, the crystals were washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. (Yield 2.93g, 63%).

The same solid, $TiCl_3(OMe)\cdot 2THF$ was produced in the reaction of $TiCl_3(O_2CPh)$ with MeOH in THF solution.

i.r. 1460(s) 1375(s) 1340(m) 1300(w) 1250(w)
1175(w) 1100(s) 1075(s) 1040(w) 1005(s)
920(m) 850(s) 720(s) 670(m) 610(m)
360(s) 305(m) cm^{-1}

^1H n.m.r. 2.05(s)(8H) 4.35(s)(8H) 4.85(s)(3H)p.p.m.

Analysis based on $TiCl_3C_9H_{19}O_3$:

	Ti	Cl	C	H
calculated:	14.81;	32.28;	32.81;	5.81%
found:	14.85	32.00	32.85	5.96

Preparation of other adducts of the type $[TiCl_2(O_2CPh)\cdot L]_2O$

$[TiCl_2(O_2CPh)\cdot EtOAc]_2O$ (0.68g, 1.02 mmol) was dissolved in benzene (50 cm^3) to form a clear yellow

solution. Pyridine (0.164 cm^3, 2.04 mmol) was added dropwise to this magnetically stirred solution, and a yellow precipitate formed immediately. The supernatant was removed, the solid was washed with petroleum ether (3 x 30 cm^3), and dried in *vacuo* for 2 hours. On standing the yellow solid gradually turned green, over one hour.

Similar procedures were followed with acetonitrile, triphenylphosphine, and triethyl phosphine, and in each case a yellow solid was isolated which slowly turned green on standing. These solids were not fully characterised because of their inhomogenity.

Preparation of $SnCl_3(O_2CMe)\cdot EtOAc$

Acetic acid (0.99cm^3, 17.2 mmol) was added dropwise to a magnetically stirred solution of $SnCl_4$ (2.0 cm^3, 17.3 mmol) in benzene (30 cm^3). The resulting colourless solution was heated to reflux temperature for 1 hour. After cooling to room temperature the solvent was removed by pumping and colourless, viscous oil resulted. This was washed with petroleum ether (2 x 30 cm^3), and then redissolved in benzene (30 cm^3). EtOAc (1.69 cm^3, 17.3 mmol) was added dropwise to this

solution, and after the solvent had been removed by pumping an amorphous solid resulted. This was heated to its melting point (65°C) under reduced pressure (0.1 mmHg) for 10 minutes. On cooling a white solid formed which was dissolved in benzene (20 cm^3), and large colourless crystals formed on standing overnight. The supernatant was removed, the crystals were washed with petroleum ether (2 x 30 cm^3), and dried in *vacuo* for 2 hours. (Yield 4.70g, 73%).

i.r. 1690(s) 1615(m) 1535(m) 1460(s) 1380(s)
1300(m) 1270(m) 1140(s) 850(w) 720(s)
675(w) 615(m) 565(m) 470(s) 340(s)
310(s) cm^{-1}

^1H n.m.r.

$CDCl_3$	1.38(t)(3H)	2.32(s)(3H)	2.42(s)(3H)	4.32(q)(2H)
C_6D_6	0.90(t)(3H)	1.30(s)(3H)	1.70(s)(3H)	3.54(q)(2H)

p.p.m.

Analysis based on $SnCl_3C_6H_{11}O_4$:

calculated:	Sn, 31.9;	Cl, 28.58;	C, 19.37,	H, 2.99%
found:	30.9	28.84	19.38	2.96

CHAPTER 4

4.0. Introduction

Another approach to the modelling of Ziegler Natta catalysts is the preparation of low oxidation state titanium compounds in which hydrides, alkyls, or even alkenes, co-ordinated to the metal are stabilized by suitable ligands. As described below (Sections 4.2, 4.3, 4.4) phosphine ligands have been employed with some success in the preparation of complexes of the Group IVA elements in oxidation states (O) and (II).

The work presented in this thesis represents a preliminary study into the viability of preparing such compounds by reactions of phosphine complexes of titanium and zirconium chlorides. Reactions of complexes of the bidentate amine ligand TMEDA have been studied for comparative purposes.

Attempts have been made to prepare stable alkyl (Sections 4.11, 4.20), hydride/borohydride (Sections 4.11, 4.13, 4.16, 4.20), and reduced (Sections 4.14, 4.20) derivatives of the titanium and zirconium complexes. While these experiments have been unsuccessful in terms of preparing and isolating the desired products, nevertheless several new adducts have been prepared, and their reactions clarified. New and convenient routes to phosphine and amine complexes have been devised, and the

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behaviour of the apparently simple phosphine adducts of $TiCl_4$ has been partly resolved. Also the syntheses of some phosphine ligands have been refined.

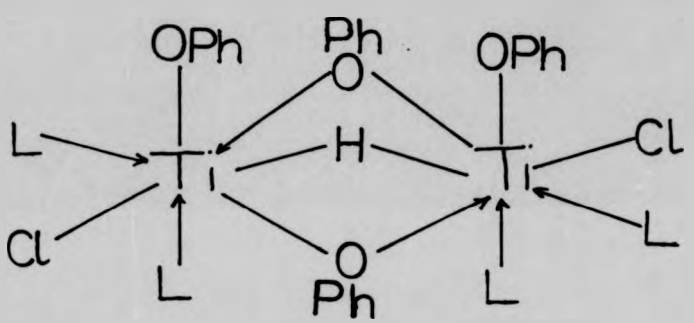
The chemistry of such compounds is discussed below (Sections 4.1, 4.2, 4.3, 4.4), along with some chemistry of $(PhO)_2TiCl_2$ (Section 4.8), which has also been studied in this respect.

4.1. Hydrides of the Group IVA Elements

Low oxidation state titanium species, such as those containing a Ti-H bond, are generally complex, air reactive, and temperature sensitive compounds, and hence they have proved difficult to characterise. This type of compound has recently been reviewed by Toogood and Wallbridge[180].

Wilkinson *et al* [181] studied the reactions of $(PhO)_2TiCl_2$ with a series of reducing agents including $NaBH_4$, Grignard reagents, and alkali metals. In these reactions a series of low valent titanium compounds are formed for which only very tentative structures could be suggested, on the basis from evidence from E.S.R. spectra, and magnetic susceptibility measurements. Titanium-hydrogen bonds were identified by their ability to form $CHCl_3$ in their reactions with CCl_4.

The product of the reaction of $(PhO)_2TiCl_2$ with an excess of $NaBH_4$ in THF solution is formulated as $[TiCl(OPh)_2(THF)]_2H$. No bands are observed in the i.r. spectrum of this solid, which are consistent with a terminal Ti-H, so a bridging hydride was proposed in the structure shown below.



The reaction of alkylating agents, such as Me_2Mg, or MeMgCl, in diethyl ether solution at -30^oC produced a yellow temperature sensitive compound, formulated as the polymer $(Ti(OPh)_2Me)_n$. This decomposes at room temperature to a diamagnetic compound with the formulation $Ti_3(OPh)_4$. No structures were proposed for these species.

A patent has described the preparation of a series of hydrides of the type $(DMPE)MH_3$ (M = Ti, Zr, Hf), by the reaction of the metal tetrabenzyl with hydrogen at high pressure (200-400 atm.) in the presence of the phosphine[182]. Evidence from

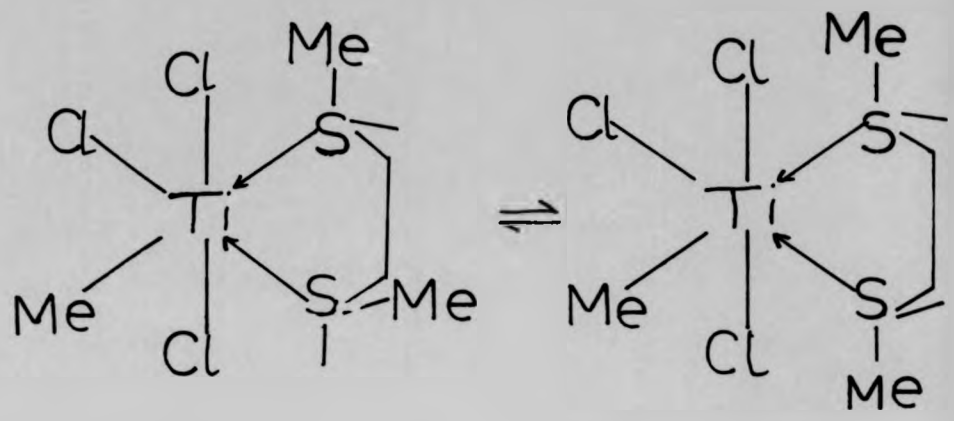
the i.r. spectra of the solids indicates that they are polymeric with bridging hydrogens.

4.2. Stabilization of Alkyl Titanium(IV) Compounds by Complexation.

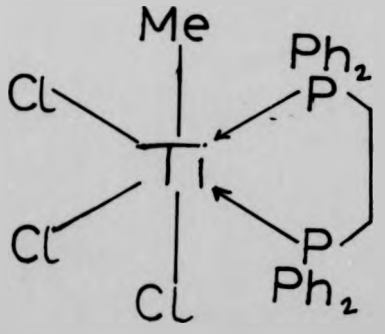
Titanium alkyl chlorides are only stable at room temperature for short periods. However, the stability of such compounds is usually enhanced by adduct formation.

The compounds $MeTiX_3$ (X = Cl, Br) form 1:2 adducts with monodentate ligands such as THF, CH_3CN and Me_2S, and 1:1 adducts with bidentate ligands, such as TMEDA, $MeOCH_2CH_2OMe$ and DPPE[183,184] in which the titanium atoms are six co-ordinate.

Complexes of $MeTiCl_3$ with bidentate ligands were assigned a *mer* structure, primarily on the basis of evidence from low temperature ^1H n.m.r. spectra of the adduct of the sulphur-bonded ligand $MeSCH_2CH_2SMe$. At room temperature one signal due to the methyl groups of the ligand is observed, but at -70^oC two separate doublets are observed which can be assigned to the methyl groups of the ligand. This spectrum is consistent with the adduct having a *mer* conformation, and the methyl groups being either *cis* or *trans* to each other, due to the slowing of inversion at sulphur[184,185].



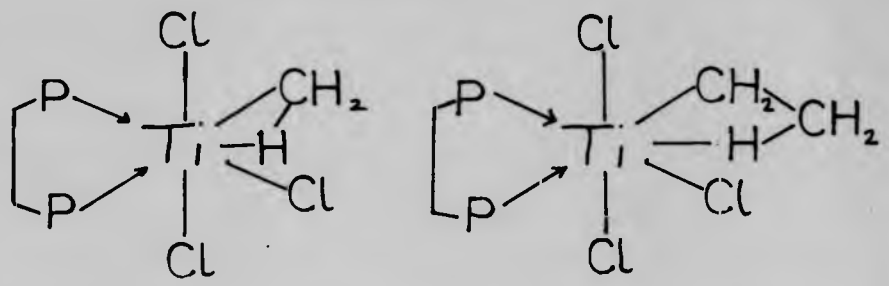
The DPPE adduct of $MeTiBr_3$ was assigned a *fac* structure since the resonances in the ^1H n.m.r. spectrum corresponding to the methyl group is a symmetrical triplet, indicating that the protons couple with two equivalent phosphorus atoms[186].



The adducts of the type $MeTiX_3 \cdot DPPE$ (X = Cl, Br) were observed to be more stable than those with other ligands, but subsequently the adducts of the related bidentate alkyl phosphine, DMPE, have been shown to be even more stable.

The alkyls, $RTiCl_3$ (R = Me, Et), decompose

rapidly at room temperature, but their DMPE adducts, $RTiCl_3 \cdot DMPE$, were shown to be sufficiently stable for structure determination by X-ray methods. Both adducts have a *mer* structure.[187,188]



The structure of $EtTiCl_3 \cdot DMPE$ provides strong evidence for an interaction between a β-hydrogen of the ethyl group and titanium. The Ti-C-C angle of 85.9° clearly indicates that the methyl group is drawn towards the titanium centre, as all previously reported M-C-C angles are in the range 108-123°. A three centred-two electron bond involving Ti, C and H was suggested to account for this interaction[187].

An interaction between titanium and an α-hydrogen is observed in $MeTiCl_3 \cdot DMPE$. The Ti-C-H angle is 70°, and the Ti-H distance, at 2.03 Å is lower than the sum of the Van der Waals' radii of these atoms. These observations were again explained in terms of a three centred-two electron bond, involving titanium, carbon, and hydrogen[188].

4.3. Low Oxidation State Compounds of the Group IVA Elements Containing Phosphine Ligands

Chatt and Watson[189] attempted to isolate a Ti(0) complex by reducing $TiCl_4$ with sodium naphthenide, in the presence of three mole equivalents of DMPE. After a succession of colour changes, black metallic titanium precipitates from this solution, indicating that species such as $[Ti(DMPE)_3]$ are not stable.

Wreford and his co-workers have succeeded in preparing a series of complexes of zero-valent Group IVA elements containing phosphine ligands. Reduction of $ZrCl_4 \cdot 2DMPE$ with an excess of sodium amalgam, in the presence of two mole equivalents of butadiene, yields the dimeric complex $[Zr(C_4H_6)_2(DMPE)]_2 \cdot DMPE$. One DMPE molecule bridges between two seven co-ordinate zirconium atoms.

$$2ZrCl_4 \cdot 2DMPE + 4C_4H_6 \xrightarrow{Na/Hg} [Zr(C_4H_6)_2(DMPE)]_2 \cdot DMPE + 8NaCl + DMPE$$

Monodentate ligands, such as PMe_3 and CO disrupt the dimer by reversible exchange[190].

$$[Zr(C_4H_6)_2(DMPE)]_2\ DMPE + 2CO \rightleftarrows 2[Zr(C_4H_6)_2(DMPE) \cdot CO] + DMPE$$

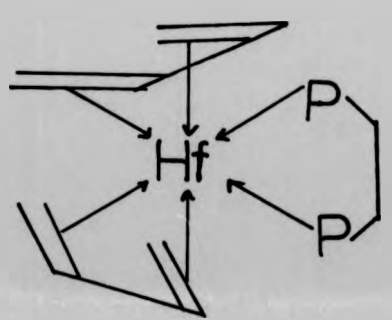
The titanium analogue of this compound, $[Ti(C_4H_6)_2(DMPE)]$, can be prepared by the same method, but this is monomeric, and remains six co-ordinate in the presence of PMe_3 or CO[191].

All these compounds catalyse the dimerization of alkenes, including ethylene and propylene, as observed by ^1H n.m.r. spectroscopy.

The same workers have developed a general method for the preparation of complexes of the type $[M(C_4H_6)_2(R_2PCH_2CH_2PR_2)]$ (M = Ti, Zr, Hf; R = Me, Et, Ph, OMe)[192].

These compounds are formed when an appropriate metal tetrachloride is treated with two mole equivalents of $Mg(C_4H_6)_2 \cdot 2THF$, in the presence of the bidentate phosphine in THF solution.

The hafnium compound $[Hf(C_4H_6)_2DMPE]$ can be prepared by this method, though it was not possible to prepare this compound by sodium-amalgam reduction of $HfCl_4 \cdot 2DMPE$ in the presence of butadiene. This adduct was characterised by X-ray diffraction methods[192].

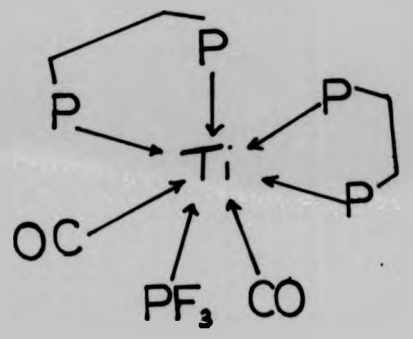


Although the ligand butadiene is clearly important in stabilizing the metals in oxidation state (0) in these compounds, the phosphines were observed to have an effect on the stability and reactivity of these compounds.

A compound of the type $[M(C_4H_6)_2DPPE]$ forms only with titanium, and no stable compounds are formed with monodentate phosphines.

As discussed above the DMPE adducts dimerize alkenes, but the $(MeO)_2PCH_2CH_2P(OMe)_2$ adduct does not react with alkenes, whereas the reaction of $[Ti(C_4H_6)_2DPPE]$ with ethylene forms a polymer. The differences in reactivity were proposed to be due to the varying abilities of the phosphines to stabilize alkene complexes of the metals[191].

High pressure carbonylation of the complex $[Ti(C_4H_6)_2DMPE]$ produces a polymeric carbonyl $[Ti(CO)_3(DMPE)_{3/2}]_n$. This reacts further with DMPE and PF_3 to form $[Ti(CO)_2PF_3(DMPE)_2]$, which has been structurally characterised by X-ray methods and shown to be an approximate capped trigonal prism[193].

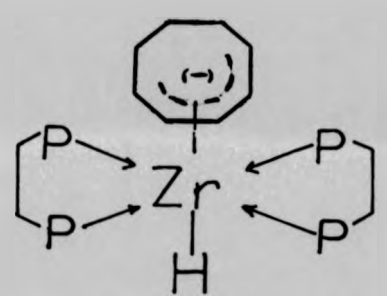


The zirconium(II) hydride $[ZrH(DMPE)_2(C_6H_7)]$ is formed by the reduction of $ZrCl_4 \cdot 2DMPE$ with sodium amalgam in the presence of 2,3 cyclohexadiene[73]. An analogous reaction takes place with 1,3 cyclooctadiene to form $[ZrH(DMPE)_2(C_8H_{11})]$.

In neither case could the hydride be detected by ^1H n.m.r. or infra-red spectroscopy, but the reactions of these compounds with methyl iodide, and acids, produced quantitative amounts of methane and hydrogen, respectively.

$$Zr - H + CH_3I \rightarrow Zr - I + CH_4$$
$$Zr - H + HCl \rightarrow Zr - Cl + HCl$$

The presence of hydride was also inferred from the crystal structure of $[ZrH(DMPE)_2(C_8H_{11})]$, which was determined by X-ray methods. The zirconium atom is in a distorted octahedral environment, with the hydride trans to the C_8H_{11} group[194].



This compound reacts with cyclooctatetraene to produce a zero valent complex $[Zr(C_8H_8)_2]_2 \cdot DMPE$[194].

The hydride compounds described above act as hydrogen transfer catalysts in that they react with solutions of 1,3·cyclohexadiene to produce equimolar amounts of benzene and cyclohexane[194].

The reactions described above indicate that reduction of $ZrCl_4 \cdot 2DMPE$ produces a fragment such as $Zr(DMPE)_2$, which may be trapped by butadiene in the form $[Zr(C_4H_6)_2DMPE]$, or it can insert into an allylic bond of compounds such as cyclohexadiene to form Zr(II) hydrides, of the type $[Zr(H(DMPE)C_6H_7]$, by an oxidative-addition reaction.

4.4. Metal Atom Routes to Phosphine Complexes of Group IVA

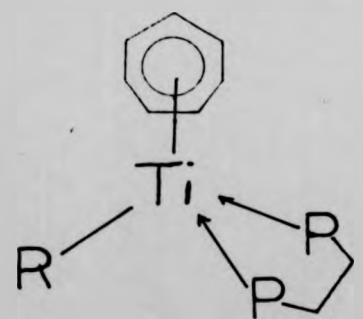
Low oxidation state phosphine complexes of the Group IVA elements can be prepared by condensing vapours of metal atoms into solutions of the phosphine.

Condensation of zirconium or hafnium vapour into toluene solutions of PMe_3 at -196^oC produces green solutions, from which the compounds $[M(C_6H_5CH_3)_2PMe_3]$ (M = Zr, Hf) can be isolated. The related compound, $[Zr(C_6H_6)_2PMe_3]$, can be prepared similarly using benzene as the solvent[195].

A bent sandwich structure was suggested for these compounds.

The same workers have prepared phosphine complexes of low-valent titanium in the reactions of $[Ti(C_6H_5CH_3)_2]$, which is prepared by condensation of titanium atoms into toluene[196].

When $[Ti(C_6H_5CH_3)_2]$ is treated with cycloheptatriene and $EtAlCl_2$ in THF solution, the dimeric complex $[(C_7H_7)TiCl\cdot THF]_2$ is formed. Phosphines disrupt this dimer to form complexes of the type $(C_7H_7)TiCl\cdot 2L$ ($L=PMe_3$, $\frac{1}{2}$DMPE), and the DMPE adduct reacts with appropriate Grignard reagents to form stable alkyls of the type $[(C_7H_7)Ti(DMPE)R]$ (R = Me, Et). The ethyl derivative has been shown by X-ray methods to have a half-sandwich structure[197].



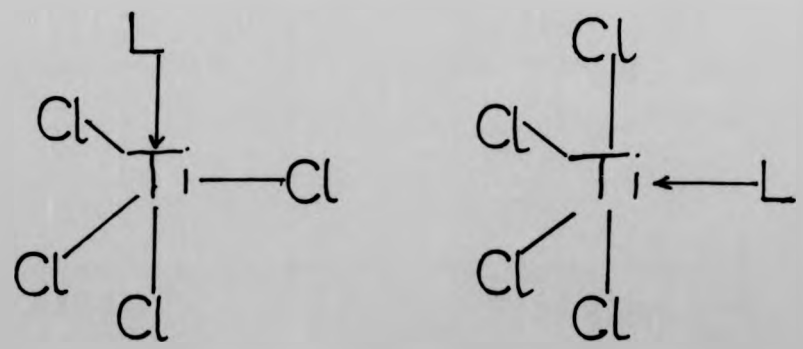
4.5. Phosphine Adducts of $TiCl_4$

The complexes of trialkyl phosphines with $TiCl_4$ were first reported as 1:2 adducts of the

type $TiCl_4 \cdot 2PR_3$ by Chatt and Hayter[198], though two adducts of phosphine itself, PH_3, had previously been reported as $TiCl_4 \cdot PH_3$ and $TiCl_4 \cdot 2PH_3$ [199].

Triphenylphosphine, PPh_3, was also reported to form both 1:1 and 1:2 adducts with $TiCl_4$. The product is dependent on the initial ratio of the reactants. The 1:1 adduct is formed if $TiCl_4$ is present in excess, whereas the 1:2 adduct is formed when the ligand is present in excess[200].

Evidence from i.r. and Raman spectra indicate that 1:1 phosphine adducts of $TiCl_4$ can have two different structures. The adducts all have a t.b.p. structure, but PMe_3 was proposed to take up an axial position, whereas PH_3, PH_2Me and $PHMe_2$ are equatorial[201].



The bidentate phosphine, DPPE, was reported to form complexes with the formulations $(TiCl_4)_2 \cdot 3L$, $TiCl_4 \cdot L$ and $(TiCl_4)_3 \cdot 2L$. The compound $TiCl_4 \cdot L$ is prepared by mixing the reactants in a stoicheiometric ratio in benzene solution. The other compounds form when the appropriate component is present in a five-fold excess. No structures were proposed for these compounds, but it was suggested that the titanium atoms may have a co-ordination number of greater than six. However molecular weight measurements indicate that more than one species may be present in the benzene solutions of these compounds.[200]

The equilibria in solutions of $TiCl_4$ phosphine adducts have been studied by ^1H and ^{31}P n.m.r. spectrocopy[38]. The ligand PMe_2Ph was chosen for this study, because the resonance of the methyl groups in ^1H n.m.r. spectra is an easily assigned doublet. When the ratio of $TiCl_4$:PMe_2Ph in CD_2Cl_2 solution is 2:1 a broad, unresolved signal due to the methyl groups of the ligand is observed in the ^1H n.m.r. spectrum at room temperature. This moves downfield and is resolved into a doublet when the ratio is increased to 8:1. This observation implies that at least two species are in equilibrium, which is fast on the n.m.r. time-scale.

At low temperature (-57°C) the signal from a solution of $TiCl_4$ and PMe_2Ph in a 2:1 ratio is resolved into two doublets, but as the ratio is increased by addition of further $TiCl_4$ both doublets move downfield, indicating that more than two species are present. A species high in $TiCl_4$ content, $(TiCl_4)_2PMe_2Ph$, was proposed to be in equilibrium with the expected 1:1 and 1:2 adducts to explain these observations.

$$(TiCl_4)_2 \cdot PMe_2Ph \rightleftharpoons TiCl_4 \cdot PMe_2Ph + TiCl_4$$
$$(TiCl_4)_2 \cdot PMe_2Ph + PMe_2Ph \rightleftharpoons 2\ TiCl_4 \cdot PMe_2Ph$$
$$TiCl_4 \cdot PMe_2Ph + PMe_2Ph \rightleftharpoons TiCl_4 \cdot 2PMe_2Ph$$

Evidence from ^{31}P n.m.r. spectra of these solutions supports this hypothesis. Only one resonance is observed in the spectra of solutions of $TiCl_4$ and PMe_2Ph mixed in varying molar ratios. The chemical shift of the resonance is dependent upon the ratio, varying between -9.0 and +45 p.p.m. as the ratio $TiCl_4$:PMe_2Ph is varied between 8:1 and 1:10.

The analogous $TiCl_4$ systems, with PEt_3 and PBu_3, were studied by ^{31}P n.m.r. spectroscopy in the course of this work, and the results are discussed in Section 4.9.

4.6. Phosphine Adducts of $TiCl_3$

Trialkyl phosphines react slowly with $TiCl_3$ in toluene at 85°C to form adducts of the $TiCl_3 \cdot 2PR_3$[202]. Molecular weight measurements indicate that the complexes are monomeric in benzene solution and thus contain five co-ordinate titanium atoms. Although the 1:2 adducts precipitate from solution E.S.R. and visible spectra indicate that a 1:3 adduct forms in solution in the presence of excess phosphine.

$$TiCl_3 \cdot 2PR_3 + PR_3 \rightleftarrows TiCl_3 \cdot 3PR_3$$

At room temperature a triplet due to the 1:2 adduct, and a quartet due to the 1:3 adduct, are observed in the E.S.R. spectrum of a solution of $TiCl_3$ and three mole equivalents of PEt_3. The relative intensity of the triplet increases as the temperature is increased and the quartet becomes more intense as the temperature is lowered. Bands at 610 and 470 n.m. in the visible spectrum of this solution show similar temperature dependence[203].

By analogy with the trimethylamine adduct $TiCl_3 \cdot 2NMe_3$, these compounds are likely to have a t.b.p. structure in which the phosphines are *trans*.

The adduct $TiCl_3 \cdot DEPE$ can also be prepared by reaction of $TiCl_3$ and the ligand over an extended period, though no properties of this compound were reported[198].

Compounds of this type have been studied in the course of this work, and are discussed in Section 4.17.

4.7. Phosphine Complexes of $ZrCl_4$ and $ZrCl_3$

Monodentate phosphines form simple *cis* adducts with $ZrCl_4$ of the type $ZrCl_4 \cdot 2PR_3$. The bidentate ligand DPPE form an analogous adduct $ZrCl_4 \cdot DPPE$[204], but DMPE forms a 1:2 complex, $ZrCl_4 \cdot 2DMPE$ in which the zirconium atoms are eight co-ordinate[73].

The phosphine adducts of $ZrCl_3$ have not been prepared by direct reaction of $ZrCl_3$ with ligands, but the compounds $[ZrCl_3(PR_3)_2]_2$ (R = Et, Pr, Bu) can be isolated by the reaction of the corresponding $ZrCl_4$ adducts, $ZrCl_4 \cdot 2PR_3$, with one mole equivalent of sodium amalgam[79]. The structure of the PBu_3 adduct has been discussed previously (Section 1.12.).

4.8. The Chemistry of $(PhO)_2TiCl_2$

In common with the alkoxides, titanium phenoxides are best prepared by the elimination of HCl from

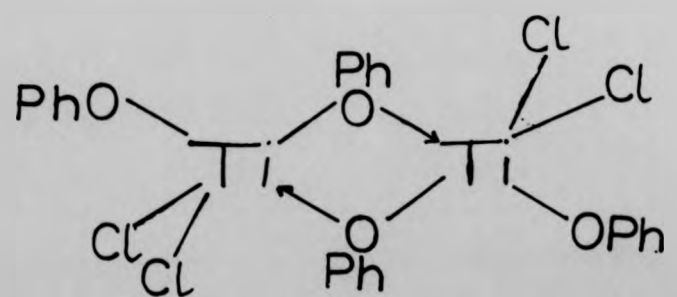
$TiCl_4$. Hence $(PhO)_2TiCl_2$ can be prepared by mixing a stoicheiometric amount of phenol with $TiCl_4$ in an inert solvent, such as CCl_4.

$$2PhOH + TiCl_4 \xrightarrow[CCl_4]{reflux} (PhO)_2TiCl_2 + 2HCl$$

Titanium tetraphenoxide can be prepared if an HCl acceptor, such as ammonia, is added to the reaction mixture.

$$4PhOH + TiCl_4 + 4NH_3 \rightarrow Ti(OPh)_4 + 4NH_4Cl$$

The structure of $(PhO)_2TiCl_2$ in the solid state has been determined by X-ray methods, and shown to be a phenoxide bridged dimer[205]. Evidence from molecular weight measurements, and ^1H n.m.r. spectra, indicates that this structure is retained in solution[181].



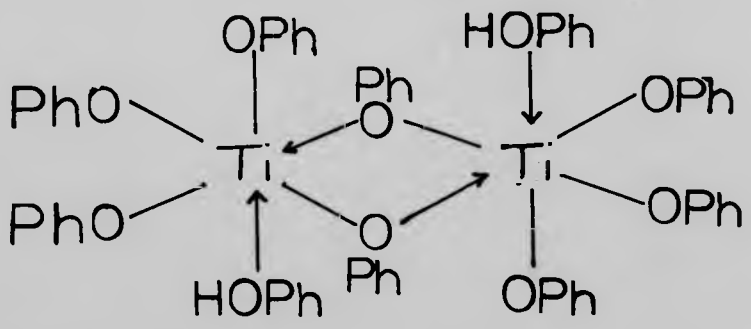
This structure is unusual in that the titanium atoms are five co-ordinate. However, in the few

adducts of $(PhO)_2TiCl_2$ which have been reported, the titanium atoms are six co-ordinate in complexes of the type $(PhO)_2TiCl_2 \cdot 2L$ (e.g. L = py)[206].

The acceptor strength of titanium alkoxy (or phenoxy) chlorides decreases as chloride is substituted by alkoxide (or phenoxide):

$$TiCl_4 > (PhO)_2TiCl_2 > Ti(OPh)_4$$

The tetraphenoxide forms adducts of the type $[Ti(OPh)_4 \cdot L]_2$. The phenol adduct has been structurally characterised by X-ray methods, and shown to be a phenoxide bridged dimer[207].



Results and Discussion

4.9. Preparation of the Phosphine Adducts of $TiCl_4$

The preparation of the bis-phosphine adducts of $TiCl_4$ was first attempted using the previously reported methods[38,198].

Dropwise addition of $TiCl_4$ to a magnetically

stirred solution of two mole equivalents of PEt_3 in toluene, benzene, Et_2O or CH_2Cl_2 solution at room temperature produced a dark red colouration. After stirring for 30 minutes, the volume was reduced by pumping. Precipitation of the adduct did not take place as readily as had previously been reported[198]. Despite attempts to follow the same procedure most preparations produced dark red oils, and only about one preparation in three produced a dark red precipitate. In these cases the supernatant was removed, the solid washed with petroleum ether, and dried in *vacuo*, until a free flowing powder was produced. The solids produced had a variable composition, but approximated to $TiCl_4 \cdot 1.8PEt_3$ by analysis.

Slight modifications of the method described above, which involved for example adding the $TiCl_4$ in a dilute solution in the reaction solvent to a solution of PEt_3 at $-20^{o}C$, did not improve the reliability of the preparation.

When similar procedures were followed with tri-n-butylphosphine no solid adduct was precipitated. It appears that the long alkyl chain of this phosphine considerably enhances the solubility of its adduct with $TiCl_4$, which may be an oil.

Solutions of $TiCl_4$ and the trialkylphosphines PEt_3 and PBu_3 in C_6D_6 and $CDCl_3$ were studied using ^{31}P n.m.r. spectroscopy in order to ascertain why the simple adducts could not be isolated in a pure form.

In a typical ^{31}P n.m.r. experiment $TiCl_4$ (0.1 cm^3), followed by the phosphine were added to the solvent (2.5 cm^3) to produce a solution in which the molar ratio of $TiCl_4$:PR_3 was 10:1. After recording the spectrum the ratio was changed by further addition of phosphine. A series of spectra were run with $TiCl_4$:PR_3 ratios varying between 10:1 and 1:10. The results are presented in the Tables below.

PEt_3

ratio $TiCl_4$:PR_3	Resonance (p.p.m.)			
	25.3	22.3	21.1	-20.0
10:1		✓	✓	x
5:1		✓	x	x
2:1		x	x	✓
1:1	✓	x	✓	
1:2	✓	x	✓	
1:5	x	x	✓	
1:10	x	✓	✓	

PBu_3

	25.7	15.9	11.7	-32.3
10:1		✓	✓	x
5:1		✓	x	x
2:1		x	x	✓
1:1	✓	x	✓	
1:2	✓	x	✓	
1:5	x	x	✓	
1:0	x	✓	✓	

Shifts rel. to 80% H_3PO_4 = 0 p.p.m.
positive values downfield

With both PEt_3 and PBu_3 a total of four separate resonances are observed in the 36.34 MHz spectra. The resonances at highest field -20.0 and -32.3 p.p.m., correspond exactly to the resonances for the unco-ordinated ligands PEt_3 and PBu_3 respectively.

On the basis that the inductive effect on a phosphine is likely to increase across the series $TiCl_4 \cdot 2PR_3 > TiCl_4 \cdot PR_3 > (TiCl_4)_2 \cdot PR_3$ the following assignments of the other resonances are proposed.

Compound	Resonance (p.p.m.)	
	R = Et	R = Bu
$(TiCl_4)_2 \cdot PR_3$	25.3	15.7
$TiCl_4 \cdot PR_3$	22.3	15.9
$TiCl_4 \cdot 2PR_3$	21.1	11.7

Thus the adducts $TiCl_4 \cdot PR_3$ and $TiCl_4 \cdot 2PR_3$, are observed in all the solutions. Unco-ordinated phosphine is observed when more than one mole equivalent of phosphine is present, whereas the complexes formulated as $(TiCl_4)_2 \cdot PR_3$ are present when less than one mole equivalent of the phosphine is present.

The spectrum of the precipitate formulated as $TiCl_4 \cdot 1.8PEt_3$ dissolved in $CDCl_3$ or C_6D_6 is similar to that of a 1:1 mixture of $TiCl_4$ and PEt_3. The resonance at 21.7 p.p.m. is most intense, being approximately 70% of the total phosphine, but resonances at 19.1 and 25.7 p.p.m. are also observed, indicating that $TiCl_4 \cdot 2PEt_3$ and $(TiCl_4)_2 \cdot PEt_3$ respectively are also present in the solution.

The assignment of the resonance observed at lowest field, to a species formulated as $(TiCl_4)_2 \cdot PR_3$, is due to Susz *et al*[38]. Their observations on similar systems are described in Section 4.5. The

most marked difference between these observations and those presented here is that only one resonance was observed in the ^{31}P n.m.r. spectra of the $TiCl_4/PMe_2Ph$ system, and a series of equilibria were deduced to exist because of the large variation in chemical shift of that signal with different ratios of the reactants. In the cases of PEt_3 and PBu_3 separate signals are observed for the species involved in the equilibria, indicating exchange rates in these systems must be slow on the n.m.r. timescale.

The following equilibria were proposed by Susz *et al* to account for their observations.

$$PR_3 + TiCl_4 \cdot PR_3 \rightleftarrows TiCl_4 \cdot 2PR_3 \quad (1)$$

$$TiCl_4 \cdot 2PR_3 + TiCl_4 \rightleftarrows 2TiCl_4 \cdot PR_3 \quad (2)$$

$$TiCl_4 \cdot PR_3 + TiCl_4 \rightleftarrows (TiCl_4)_2 \cdot PR_3 \quad (3)$$

The observations presented here are also consistent with such a system, though a more complete description of the system may also require consideration of two further equilibria:

$$PR_3 + TiCl_4 \rightleftarrows TiCl_4 \cdot PR_3 \quad (4)$$

$$(TiCl_4)_2 \cdot PR_3 + PR_3 \rightleftarrows 2TiCl_4 \cdot PR_3 \quad (5)$$

Thus when the concentration of $TiCl_4$ is high, equilibrium (4) is moved to the right, and no free phosphine is observed in the ^{31}P n.m.r. spectra of such solutions. Similarly when phosphine is present in excess, equilibrium (5) is moved to the right, and the species $(TiCl_4)_2 \cdot PR_3$ is not observed in these conditions.

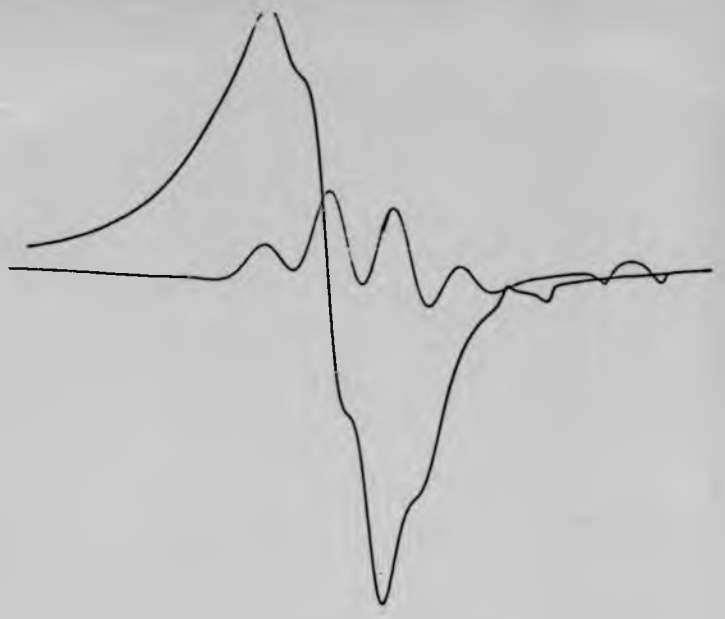
In high resolution ^{31}P n.m.r. spectra (163 MHz), the signals corresponding to $TiCl_4 \cdot 2PR_3$ in a 1:1 mixture of $TiCl_4$ and ligand were resolved into two signals at 11.7 and 11.9 p.p.m., and 19.1 and 21.2 p.p.m. These resonances are tentatively assigned to the *cis* and *trans* isomers of the adducts.

Unfortunately it proved difficult to quantify the relative amounts of the individual species in solution. A feature of the spectra is that all the resonances are broad and hence the integrals are unreliable. The resonances due to the free phosphine are particularly wide ($\Delta_{\frac{1}{2}}$ = 7 p.p.m.).

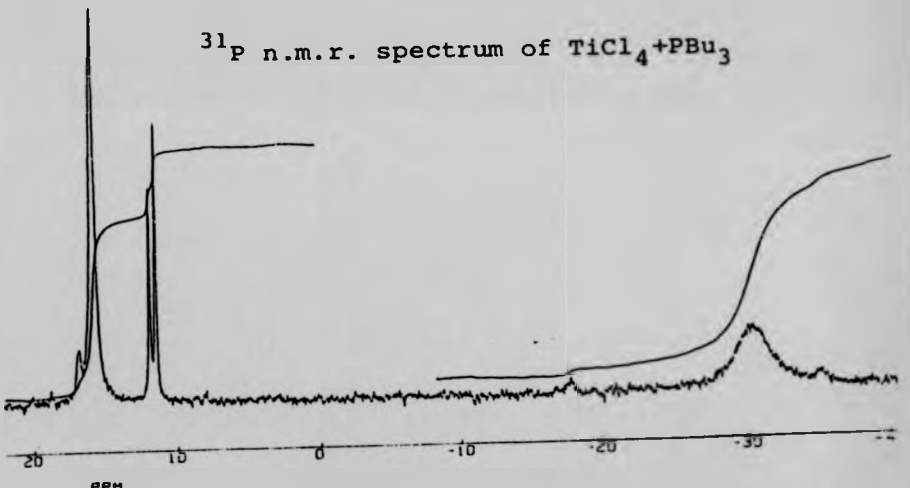
The fact that these resonances are much broader than the resonances corresponding to co-ordinated phosphines suggests that there was a paramagnetic species present in solution. Exchange broadening would produce signals of similar width, but this possibility may be eliminated because the spectra are unchanged at low temperatures (-70°C).

E.S.R. spectrum of

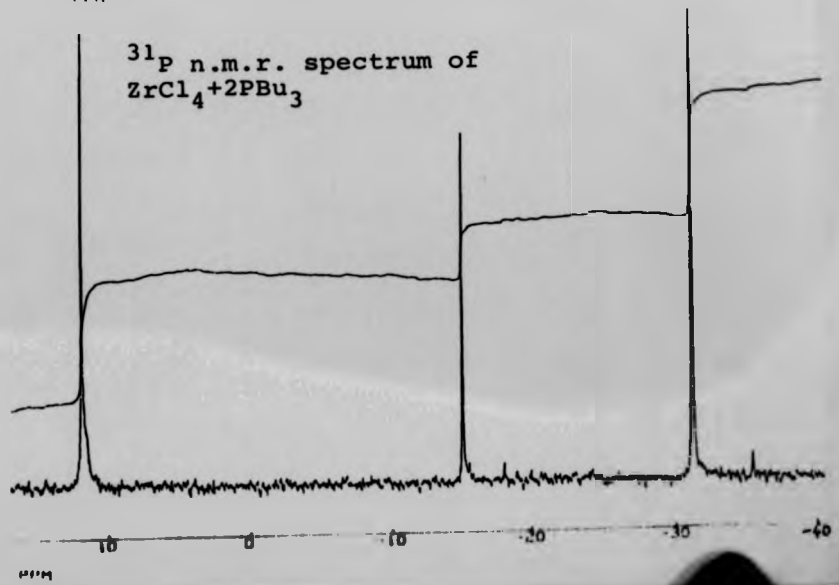
$TiCl_4+2PBu_2$



^{31}P n.m.r. spectrum of $TiCl_4+PBu_3$



^{31}P n.m.r. spectrum of
$ZrCl_4+2PBu_3$



The E.S.R. spectrum of a solution of equimolar amounts of $TiCl_4$ and PBu_3, at -196°C, confirms the presence of a paramagnetic species. A triplet is observed at 2.95g, which is very similar to that reported for $TiCl_3 \cdot 2PMe_3$[203]. Reduction of Ti(IV) to Ti(III) by phosphine has been proposed previously, but no evidence was presented[200]. In this work reduction of Ti(IV) to Ti(III) took place even when dilute (0.1M) solutions of $TiCl_4$ and PBu_3 were mixed slowly at -50°C, and therefore seems unavoidable.

These observations suggest that interactions in solutions of $TiCl_4$ and trialkyl phosphines are complex. Several species such as $TiCl_3 \cdot 2PR_3$, $TiCl_4 \cdot PR_3$, $TiCl_4 \cdot 2PR_3$, and $(TiCl_4)_2 \cdot PR_3$ co-exist, so it may be reasonable that the solids which precipitate from such solutions are not simple.

4.10. Preparation of the $TiCl_4$ Adducts of DMPE and DBPE

The preparations of the $TiCl_4$ adducts of the bidentate phosphine ligands DMPE and DBPE are more straightforward than those of the monodentate trialkylphosphines.

When one mole equivalent of DMPE is added dropwise to a stirred solution of $TiCl_4$ in toluene at 0°C, an orange precipitate forms immediately. Removal of the supernatant, washing with petroleum ether, and

drying in *vacuo* yields a free-flowing powder.

When a similar procedure is followed with DBPE, only a red oil precipitates from the toluene solution. After removing the orange supernatant pumping on the oily residue for 6 hours did not produce a solid product. However, addition of petroleum ether to the oil, and stirring for 72 hours, produces an orange powder, which can be recovered as above. Analysis of these two solids confirms their composition as 1:1 adducts.

The ^{31}P n.m.r. spectra of each of these adducts in $CDCl_3$ solution shows only one resonance ($TiCl_4$·DMPE, 10.1; $TiCl_4$·DBPE, 39.0 p.p.m.), in contrast to the spectra of the $TiCl_4$ adducts of the monodentate phosphines. The compounds therefore appear to be simple 1:1 adducts in solution also, with two donor atoms in *cis*-positions around the central six co-ordinate metal atom.

4.11. Reactions of the DMPE and DBPE Adducts of $TiCl_4$

The complexes of $TiCl_4$ with bidentate phosphines were chosen for further study, because the ^{31}P n.m.r. experiments had shown that these compounds are less labile than the adducts of monodentate phosphines.

One mole equivalent of $LiBH_4$ was added to a

stirred solution of $TiCl_4 \cdot DMPE$ in THF. The orange solution gradually turned green over one hour. After stirring overnight and removing the solvent, a green precipitate was obtained. After extraction into hot toluene, and filtration, a brown precipitate formed on cooling. Comparison of this solid with a prepared authentic sample showed it to be $TiCl_3 \cdot DMPE$.

$$TiCl_4 \cdot DMPE + LiBH_4 \rightarrow TiCl_3 \cdot DMPE + LiCl + \tfrac{1}{2}H_2 + \tfrac{1}{2}B_2H_6$$

The compound $TiCl_3 \cdot DMPE$ was also formed when $TiCl_4 \cdot DMPE$ was treated with one mole equivalent of sodium amalgam in THF solution.

The $TiCl_3$ adduct of DMPE was not a convenient material for further study, as it is insoluble in common solvents. The adduct $TiCl_3 \cdot DBPE$ was therefore prepared, and proved to be a more soluble material.

Treatment of $TiCl_4 \cdot DBPE$ with either $LiBH_4$ or sodium amalgam, in procedures identical to those described above, or direct reaction of $TiCl_3$ with DBPE, yields the green solid adduct $TiCl_3 \cdot DBPE$. This dissolves in THF.

Attempts were made to replace the chlorides by hydride/borohydride groups. Thus addition of one mole equivalent of $LiBH_4$ to a stirred solution of

$TiCl_3$·DBPE in THF caused the solution to darken, though no precipitate was formed. On pumping the solution to dryness a dark oil remained. Extraction with hot benzene yielded a brown powder. The ^{31}P n.m.r. spectrum of the clear benzene extract shows one strong resonance at -27.9 p.p.m. which corresponds to unco-ordinated DBPE. It was concluded that the phosphine does not remain co-ordinated under these conditions, and the product of the reaction is probably the decomposition product of a Ti(III) borohydride, which are known to be unstable at room temperature.[180] This reaction was not investigated further.

Free phosphine is also detected after the products of the reaction of $TiCl_3$·DBPE with one mole equivalent of methyl lithium in Et_2O solution was isolated, as described above. It does not appear possible to prepare a stable compound of the type $MeTiCl_2$·DBPE by this method.

4.12. Preparation of Phosphine Adducts of $ZrCl_4$

The triethyl phosphine adduct of $ZrCl_4$ was prepared by adding two mole equivalents of PEt_3 to a stirred suspension of freshly prepared $ZrCl_4$ in benzene. The $ZrCl_4$ dissolves immediately to give a clear, colourless solution.

After filtering, reduction of the volume by pumping, and standing overnight, white crystals of $ZrCl_4 \cdot 2PEt_3$ formed in the solution. The ^{31}P n.m.r. spectrum of these crystals in benzene solution shows a single resonance at 21.8 p.p.m.

When a similar procedure was followed with PBu_3 no solid formed, and removal of all the solvent leaves a very viscous yellow oil. The ^{31}P n.m.r. spectrum of this oil in benzene solution is a single resonance at 10.8 p.p.m. However, a spectrum of a reaction mixture in which all the solid $ZrCl_4$ had not dissolved contains three resonances at 10.8, -15.0 and -32.3 p.p.m. Thus the solution contains unco-ordinated phosphine together with what is presumably the bis-phosphine adduct, and another species which is responsible for the signal at -15.0 p.p.m. This is tentatively assigned to species of the type $ZrCl_4 \cdot 3PBu_3$, or $ZrCl_4 \cdot 4PBu_3$.

The adduct $ZrCl_4 \cdot 2DMPE$ was prepared by the previously reported method[73]. The unreported DBPE adduct was also prepared by a similar method. Thus two mole equivalents of DBPE were added slowly to a stirred suspension of $ZrCl_4$ in toluene. The $ZrCl_4$ dissolved slowly when the solution was heated to 80°C, and after filtering a solid precipitated immediately on cooling the filtrate.

This solid was formulated as $ZrCl_4 \cdot DBPE$ on the basis of analytical data. It was only sparingly soluble in common solvents, but sufficiently soluble in benzene solution to obtain a ^{31}P n.m.r. spectrum which shows one resonance at 37.8 p.p.m.

The zirconium atoms in this complex are probably six co-ordinate in $ZrCl_4 \cdot 2DMPE$. This may be due to the steric requirements of the longer alkyl chains. The low solubility of $ZrCl_4 \cdot DBPE$ compared with $ZrCl_4 \cdot 2DMPE$ implies that the eight co-ordinate species containing two ligands are more soluble than six co-ordinate species containing one ligand, despite the butyl-containing ligand having apparently greater solublizing properties.

4.13. Reactions of the Phosphine Adducts of $ZrCl_4$

When the solution formed by stirring $ZrCl_4$ with two mole equivalents of PBu_3 in toluene, was mixed with one mole equivalent of $LiBH_4$ the mixture became dark red on stirring for 48 hours, and a white precipitate formed. The solution was filtered and left to stand at $-20^{o}C$. No solid precipitated so the solvent was removed by pumping, and a red oil resulted. This was completely extracted into pentane. A solid did not precipitate

from this solution and the product remained intractable. The ^{31}P n.m.r. spectrum of the pentane solution is complex. The main feature of the spectrum is a resonance centred at -8.7 p.p.m., which was very broad ($\Delta_{\frac{1}{2}}$ = 10 p.p.m.), but there are less intense signals at -17.3, -14.9, -2.9 and 13.9 p.p.m.

Interestingly, when the adduct $ZrCl_4 \cdot 2PEt_3$ was treated with $LiBH_4$ under the same conditions as described above, no reaction was observed. The solution remained colourless after stirring for 14 days, and after filtration $ZrCl_4 \cdot 2PEt_3$ was recovered unchanged.

When a solution of $ZrCl_4 \cdot 2DMPE$ in toluene was treated with one mole equivalent of $LiBH_4$ no reaction was observed, and the adduct was re-crystallized unchanged from the solution. This may have been due to the insolubility of $LiBH_4$ in toluene, so the same reaction was repeated with THF as the solvent. A white precipitate formed over one hour. The supernatant was removed, and shown to contain free DMPE from its ^{31}P n.m.r. spectrum which showed a single resonance at -47.9 p.p.m. The solid residue proved insoluble in all common solvents, except water, in which it dissolves.

An experiment in which $LiBH_4$ was added to $ZrCl_4 \cdot$ 2DMPE in an n.m.r. tube, showed that the intensity

of the signal corresponding to co-ordinated phosphine before reaction was close to that of free phosphine after reaction. This indicates that two equivalents of DMPE are displaced by borohydride, and the white solid is probably a mixture of a zirconium chloroborohydride and LiCl. The i.r. spectrum of the solid shows a broad band between 2400 and 2500 cm^{-1} confirming the presence of the borohydride group.

4.14. Reactions of Phosphine Adducts of $ZrCl_4$ with Sodium Amalgam

The reactions of bisphosphine adducts of $ZrCl_4$ with one mole equivalent of sodium amalgam were investigated by Schrock *et al*[79]. Their observations have been discussed in Section 1.12.

When $ZrCl_4 \cdot 2DMPE$ was mixed with one mole equivalent of DMPE in benzene, or THF, solution, and then shaken with an excess of sodium amalgam a green solution was produced over approximately 30 minutes. The colour gradually increased in intensity and changed to red. After shaking for a further 12 hours, the solution proved to be extremely air sensitive, and was best handled in an argon atmosphere. The solution was removed from the amalgam and filtered through a celite pad.

The celite had to be pretreated by being heated to 120°C under reduced pressure, or significant decomposition took place during this procedure. After removal of the solvent a red oil remained. The oil could be extracted into pentane, but no solid could be precipitated from this solution, even after standing at -20°C for 3 months. The solution appeared to degrade over this time; the colour became much less intense, and a fine black precipitate formed. This was isolated by filtration, and appeared to be zirconium metal.

The red species present in solution is proposed to be of the type $Zr(DMPE)_n$ (where n is probably 3, 3.5 or 4). A zirconium (0) species would be very air reactive, and could precipitate zirconium metal as it decomposed.

The ^{31}P n.m.r. spectrum of this solution shows two signals. The major resonance at -47.9 p.p.m. corresponds to free DMPE, but a minor signal is observed at -2.5 p.p.m., which could be due to the zirconium (0) species present in solution, though it is close to the signal observed for the adduct $ZrCl_4 \cdot 2DMPE$ (-1.2 p.p.m.).

As it proved difficult to isolate the species present in solution its characterisation was attempted by the preparation of derivatives.

The preparation of the known compound

$[Zr(C_4H_6)_2(DMPE)]$[190] was attempted by bubbling butadiene gas into the red benzene solution. The solution rapidly became very hot, the red colour was discharged and a white solid precipitated. As the compound $[Zr(C_4H_6)_2(DMPE)]$ was reported to be blue in benzene solution it was concluded that this adduct does not form under these conditions, and that polymerization of the butadiene takes place.

A further attempt was made to react the red solution with other reagents, namely cyclopentadiene, and pentamethylcyclopentadiene, in an attempt to produce compounds such as Cp_2ZrH_2 by oxidative-addition reactions. When two mole equivalents of C_5H_6 or C_5Me_5H were added to red solutions of $[Zr(DMPE)_n]$ no change in the solution was observed over four weeks, even after the solutions had been heated to reflux for 24 hours. It was concluded that such reactions do not take place. Surprisingly, no reaction was observed when pyrrole, or iodobenzene, were added to the red solution. When an excess of methyl iodide was added to the red solution an immediate reaction was observed. The solution quickly became colourless, and a white precipitate formed. However, the i.r. spectrum of this solid is identical to that of an authentic sample of

$(Me_3PCH_2CH_2PMe_3)I_2$, and no species such as ZrI_4 could be detected. Also no reaction was observed when chlorobutane was added to the red solution even after standing for 4 weeks.

Therefore it must be concluded that the species present in the red solution formed by the reduction of $ZrCl_4 \cdot 2DMPE$, in the presence of excess DMPE, remains uncharacterised . This is largely due to its high solubility, and extreme air sensitivity, which makes its handling very difficult. The limited evidence presented here does suggest that the species may be a zirconium (O) species of the type $[Zr(DMPE)_n]$.

The reaction of $ZrCl_4 \cdot 2DMPE$ with one mole equivalent of sodium amalgam in benzene solution is slow. The colourless solution becomes pale green on shaking for an hour, but on standing the solution became colourless again as the green product precipitated onto the amalgam. It was not possible to extract the product from the amalgam with solvents such as THF or diethyl ether. The low solubility of this compound was consistent with the reported properties of $[ZrCl_3(PMe_3)_2]_2$.

However, when a similar procedure was followed with the adduct $ZrCl_4 \cdot DBPE$ the product of reduction was also totally insoluble in solvents such as toluene, benzene, THF and diethyl ether. Therefore it is

concluded that although the size of the alkyl chain of the phosphine is important in determining the solubility of the adducts of the monodentate phosphines, $[ZrCl_3(PR_3)_2]_2$[79], the lability of these systems must also enhance the solubility of the adducts. The adducts of the bidentate phosphines which are probably formed in the reactions described above are unlikely to be labile, and have low solubility regardless of the alkyl chain.

The preparation of the amine analogue of $[ZrCl_3(PBu_3)_2]_2$ was attempted. Two mole equivalents of tributylamine were added to a suspension of $ZnCl_4$ in toluene. The solid dissolved immediately to give a clear colourless solution, but on standing the solution became pale green, indicating that the amine reduced Zr(IV) to Zr(III) to some extent. The slightly coloured solution was shaken with one mole equivalent of sodium amalgam, and quickly became more intensely coloured. After 4 hours the solution was removed from the amalgam, but on standing it became colourless as a grey precipitate formed. This solid proved to be insoluble in all common organic solvents, and analysis indicated that its chloride content is much higher, and its carbon and hydrogen content much lower, than

expected for an adduct such as $ZrCl_3 \cdot 2NBu_3$. Therefore it is concluded that the solid is an intimate mixture of such an adduct and NaCl, which could not be separated.

4.15. Preparation of the TMEDA Adducts of $ZrCl_4$ and $TiCl_4$

Some chemistry of the $ZrCl_4$ adduct of the nitrogen analogue of DMPE, $Me_2NCH_2CH_2NMe_2$ (TMEDA) was investigated for comparison with the compound $ZrCl_4 \cdot 2DMPE$.

The adduct $ZrCl_4 \cdot TMEDA$ was prepared as previously reported[204], by adding one mole equivalent of TMEDA to a stirred suspension of $ZrCl_4$ in benzene. The $ZrCl_4$ did not dissolve, but after 7 days the solid isolated, by removal of the solvent, washing with petroleum ether and drying in *vacuo* analysed as $ZrCl_4 \cdot TMEDA$. Its i.r. spectrum was identical to that previously reported for this adduct[204]. A more convenient preparation of this adduct was attempted by adding one mole equivalent of TMEDA to a stirred solution of $ZrCl_4$ in EtOAc. A white precipitate, which forms immediately was isolated by the procedure described above. However, the i.r. spectrum of this solid was different from $ZrCl_4 \cdot TMEDA$, in that the major

Zr-Cl stretching band is observed at 300 cm^{-1}, rather than 340 cm^{-1}. No bands consistent with the presence of EtOAc in the solid were observed, and it analysed as $ZrCl_4 \cdot 1.5TMEDA$. This solid was also the product when the initial ratio of $ZrCl_4$:TMEDA in the reaction mixture varied between 1:0.5 and 1:5.

The adduct $ZrCl_4 \cdot 1.5TMEDA$ proved to be insoluble in all common solvents including THF and DMSO. Studies on this compound were therefore discontinued.

When one mole equivalent of TMEDA was added to a stirred solution of $TiCl_4$ in petroleum ether a yellow precipitate formed immediately. The supernatant was removed, the solid washed with further petroleum ether, and dried in *vacuo*. This solid, characterised on the basis of analytical data as $TiCl_4 \cdot TMEDA$ proved to be soluble in THF so its reaction with $LiBH_4$ was investigated in this solvent.

4.16. Reaction of $TiCl_4 \cdot TMEDA$ with $LiBH_4$

The addition of one mole equivalent of $LiBH_4$ to a yellow, stirred solution of $TiCl_4 \cdot TMEDA$ in THF caused the solution to turn first green, and then blue on stirring overnight. A white

precipitate was also observed beneath the blue solution. The solution was filtered, and the volume was reduced by pumping. On standing overnight at -20°C a blue solid formed. Bands between 2400 and 2500 cm^{-1} in the i.r. spectrum of this solid indicated that there was a borohydride group present in the solid. Therefore the solid was extracted into hot toluene and filtered. On cooling blue crystals precipitated from the toluene solution. Borohydride bands are absent from the i.r. spectrum of these crystals, but bands at 870 and 1020 cm^{-1} are consistent with the presence of co-ordinated THF, and bands at 1165 (CH_3 rocking) and 1065 (CN stretching) cm^{-1} are consistent with the presence of co-ordinated TMEDA. Analytical data is consistent with the formulation of this compound as $TiCl_3 \cdot TMEDA \cdot THF$.

The reaction of TMEDA with $TiCl_3 3THF$ in benzene solution has been reported to produce the complex $TiCl_3 \cdot 2TMEDA \cdot THF$[208]. It was proposed that TMEDA is unidentate in this compound on the basis that bands corresponding to unco-ordinated TMEDA were observed in the i.r. spectrum of this solid.

Comparison of the i.r. spectra of the two solids $TiCl_3 \cdot TMEDA \cdot THF$ and $TiCl_3 \cdot 2TMEDA \cdot THF$ confirms that they are different compounds.

When $TiCl_3 \cdot TMEDA \cdot THF$ was left under reduced pressure for 4 hours the crystals became amorphous and the i.r. spectrum of the resulting grey solid did not show any bands at 870 and 1020 cm^{-1}, indicating the absence of THF. Analytical data confirmed that this solid was $TiCl_3 \cdot TMEDA$.

$$TiCl_4 \cdot TMEDA \xrightarrow[THF]{LiBH_4} TiCl_3 \cdot TMEDA \cdot THF \rightarrow TiCl_3 \cdot TMEDA$$

4.17. Preparation of the Bidentate Phosphine Adducts of $TiCl_3$

The brown DEPE adduct of $TiCl_3$ was reported to have been prepared by the prolonged action of DEPE on $TiCl_3$ in benzene[202]. This is not an entirely satisfactory method as neither $TiCl_3$ nor the adduct were soluble in the reaction solvent, and the reaction time was long.

The $TiCl_3$ adduct of DMPE was prepared in this work by the slow addition of one mole equivalent of the phosphine to a stirred solution of $TiCl_3$ in EtOAc. The solution became dark, and a brown solid precipitated when the volume of the solution was reduced by pumping. The recovered solid was shown by analysis to be the 1:1 adduct $TiCl_3 \cdot DMPE$.

The 1:1 DBPE adduct was prepared by a similar procedure to that described above, except that

solid did not precipitate when nearly all the EtOAc had been removed by pumping. The addition of petroleum ether to the resulting oil precipitated the 1:1 adduct, $TiCl_3$·DBPE as a green solid.

Both solids are very air reactive, being instantly oxidized on exposure to air, and both were found to be insoluble in solvents such as benzene, toluene and Et_2O. Bands due to the presence of EtOAc are absent in the i.r. spectra of both the DMPE and DBPE adducts, which showed adsorptions from the Ti-Cl stretching modes at 380 and 350 cm^{-1} respectively.

4.18. Studies Based on $(PhO)_2TiCl_2$

The reactions of the phosphine adducts of $TiCl_4$ and $TiCl_3$ with reducing agents such as $LiBH_4$ did not produce stabilized low oxidation state compounds or hydrides. As titanium phenoxide bonds are less labile than titanium chloride bonds it is possible that reactions of reducing agents with adducts of $(PhO)_2TiCl_2$ may produce more stable compounds.

Preparation of the Phosphine Adducts of $(PhO)_2TiCl_2$

(i) PEt_3

The addition of two mole equivalents of PEt_3 to a stirred, red solution of $(PhO)_2TiCl_2$ yielded a red oil precipitate. The red oil proved to be immiscible with petroleum ether and no solid could be recovered even after removing the petroleum ether and pumping for a further 6 hours.

Similar intractable oils were produced when either toluene, Et_2O, THF or $CHCl_3$ were used as the initial reaction solvent.

(ii) PBu_3

Reaction of $(PhO)_2TiCl_2$ with PBu_3 also produced intractable oils.

(iii) PMe_3

When two mole equivalents of PMe_3 were distilled into a stirred solution of $(PhO)_2TiCl_2$ in benzene, using a vacuum line, the red solution slowly turned orange. An orange precipitate formed very slowly over a period of one month. On the basis of analytical data the dry solid was formulated as $(PhO)_2TiCl_2 \cdot 2PMe_3$.

(iv) PPh_3

The PPh_3 adduct of $(PhO)_2TiCl_2$ was formed when two mole equivalents of PPh_3 in Et_2O solution were added to a stirred solution of $(PhO)_2TiCl_2$ in Et_2O. A red oil formed during the mixing, but golden yellow crystals of the adduct $(PhO)_2TiCl_2 \cdot 2PPh_3$ could be recovered from the supernatant by addition of petroleum ether.

(v) DPPE

When one mole equivalent DPPE was added to $(PhO)_2TiCl_2$ in benzene solution the yellow product $(PhO)_2TiCl_2 \cdot$DPPE could be isolated by the procedure described for the PPh_3 adduct.

(vi) DMPE

The addition of one mole equivalent of DMPE to a stirred solution of $(PhO)_2TiCl_2$ caused the solution to turn orange, and a precipitate formed when the volume of the solution was reduced by pumping. Analytical data was consistent with the formulation of this orange solid as $(PhO)_2TiCl_2 \cdot$DMPE.

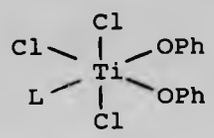
^{31}P n.m.r. spectra

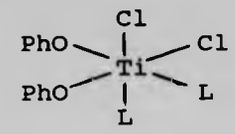
Data from the ^{31}P n.m.r. spectra of the phosphine adducts of $(PhO)_2TiCl_2$ in $CDCl_3$ solution are presented in the Table below.

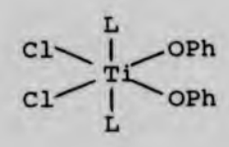
Phosphine	Resonances (p.p.m.)
PBu_3	0.8 (70) 5.6 (30)
PMe_3	65.6
PPh_3	1.8
DPPE	3.7 (70) 14.5 (30)
DMPE	-5.5

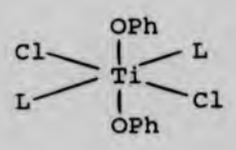
Caption: shifts are relative to 80% H_2PO_4 = 0 p.p.m., downfield shifts being positive
figures in brackets are relative intensities

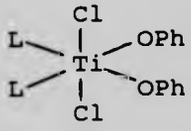
Several geometrical isomers of complexes of the type $(PhO)_2TiCl_2 \cdot 2L$ are possible, as shown below:

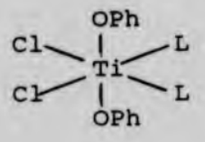
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

The ^{31}P n.m.r. spectra of the adducts of PMe_3, PPh_3 and DMPE each show only one resonance. Two resonances, in the approximate ratio of 7:3, are observed in the spectra of $(PhO)_2TiCl_2 \cdot$DPPE, and the PBu_3 adduct (which was only identified in solution, and not isolated). If only one isomer of these adducts was present in solution, then a 1:1 ratio would be expected.

The resonances in the spectrum of the DPPE adduct at -30°C are narrower than those observed in the room temperature spectrum, indicating that an exchange process is taking place. This was not observed in the spectra of $(PhO)_2TiCl_2 \cdot 2PBu_3$, but this may have been due to the presence of a paramagnetic impurity, as it has already been demonstrated that PBu_3 can reduce Ti(IV) to Ti(III) (Section 4.9.).

These observations suggest that these adducts of $(PhO)_2TiCl_2$ adopt the conformations (e) and (f), and that the two isomers are in equilibrium.

The monodentate ligands PMe_3 and PPh_3 are likely to adopt either of the conformations (c) or (d), and both are bulky and hence are likely to be *trans* for steric reasons.

The adduct $(PhO)_2TiCl_2 \cdot$DMPE is constrained to adopt one of the conformations (a), (b), (e) or (f). It is unlikely that the complex adopts the conformations (a) and (b), since in these cases two ^{31}P n.m.r. resonances would be expected as the phosphorus atoms are *trans* to different groups in these structures. Hence the DMPE adduct is likely to adopt either of the structures (e) or (f).

The differences between the DPPE and DMPE adducts may be explained in terms of two factors.

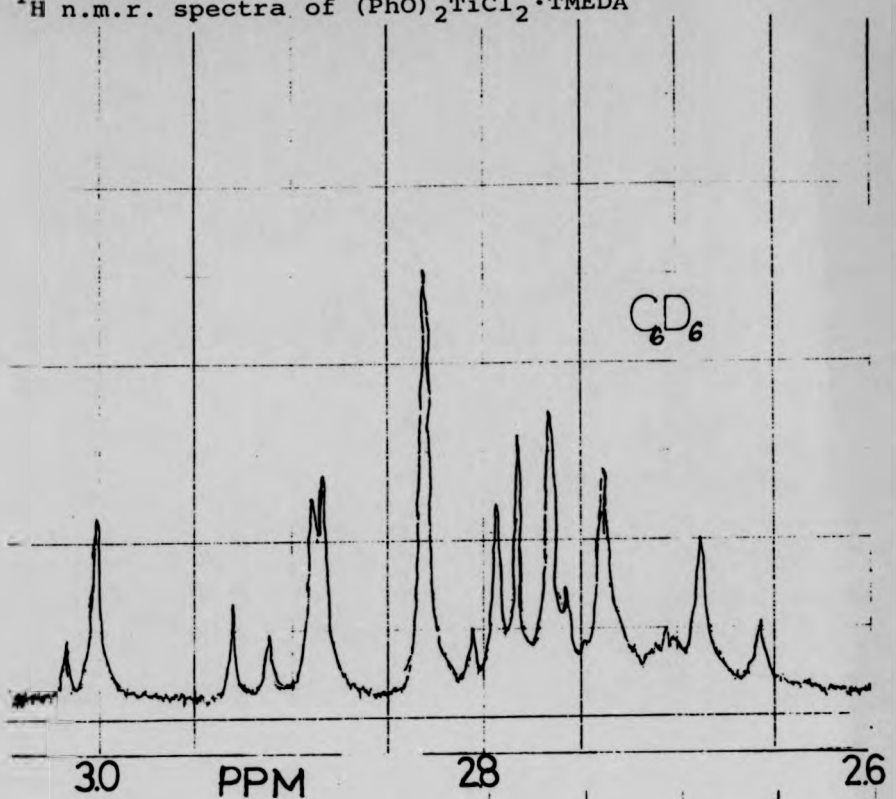
Firstly, conversion of one isomer to another (e.g. (c) to (f)) probably proceeds via a five co-ordinate intermediate which is formed by breaking of a titanium phosphorus bond. The alkyl phosphine DMPE is a stronger donor than DPPE and hence the Ti-P bonds will be less easily broken in this case. Secondly, DMPE is less bulky than DPPE so there may be less steric strain on the system, which contributes to the lability of the Ti-P bonds, in this case.

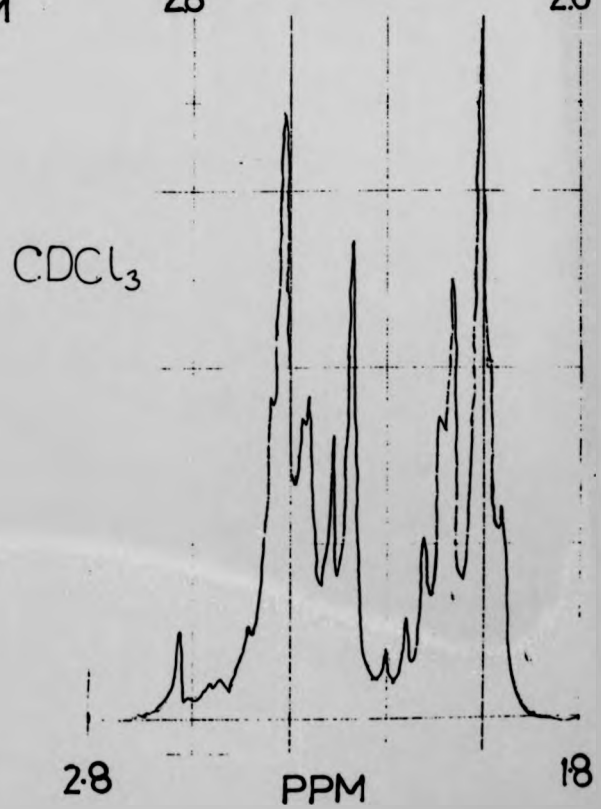
4.19. Preparation of the TMEDA Adduct of $(PhO)_2TiCl_2$

When one mole equivalent of TMEDA was added to a stirred solution of $(PhO)_2TiCl_2$ in Et_2O, an orange solid precipitated from the solution overnight. After washing with petroleum ether, and drying in *vacuo*, analytical data is consistent with the formulation of this orange solid as $(PhO)_2TiCl_2 \cdot TMEDA$.

The ^1H n.m.r. spectrum of this solid in both benzene and $CDCl_3$ solutions is very complicated. At least fifteen different resonances are observed in the regions 2.6 - 3.1 p.p.m. (benzene) and 1.9 - 2.8 p.p.m. ($CDCl_3$), where signals due to the protons of TMEDA would be expected in these solvents.

^{1}H n.m.r. spectra of $(PhO)_2TiCl_2 \cdot TMEDA$





This implies that several of the possible isomers of $(PhO)_2TiCl_2 \cdot TMEDA$ are present in solution, but it is not possible to resolve them.

4.20. Reactions of the Adducts of $(PhO)_2TiCl_2$

As previously discussed (Section 4.1) Wilkinson *et al* have found that the reaction of $(PhO)_2TiCl_2$ with reducing agents produced complex species which were not easily characterised[181]. It was thought that analogous reactions of the adducts of $(PhO)_2TiCl_2$ would produce simpler, and more stable species, which might prove easier to characterise. The action of $LiBH_4$ on some of these adducts was therefore studied.

Reaction of $(PhO)_2TiCl_2 \cdot DPPE$ with $LiBH_4$

A red solution of $(PhO)_2TiCl_2$ in THF turned green quickly on the addition of four mole equivalents of $LiBH_4$. After stirring for 4 hours and pumping to dryness the green residue was extracted into hot benzene. The green solution was filtered and on cooling white crystals formed in the filtrate.

Comparison of these crystals with an authentic sample showed them to be the unco-ordinated ligand DPPE.

The reaction of the analogous PPh_3 adduct, $(PhO)_2TiCl_2 \cdot 2PPh_3$, with $LiBH_4$, following an identical procedure to that described above, also produced a crystalline sample of the free ligand.

Reaction of $(PhO)_2TiCl_2 \cdot$DPPE with Sodium Amalgam

The addition of a red solution of $(PhO)_2TiCl_2 \cdot$ DPPE in Et_2O to an excess of sodium amalgam caused the solution to be decolourized immediately. After shaking for 30 minutes the solution was decanted from the amalgam and filtered. On standing white crystals of DPPE formed in the solution.

The reaction of $(PhO)_2TiCl_2 \cdot 2PPh_3$, with sodium amalgam, following the procedure described above, also produced the unco-ordinated ligand, PPh_3.

Reaction of $(PhO)_2TiCl_2 \cdot$DMPE with $LiBH_4$

A green solid precipitate formed when $(PhO)_2TiCl_2$ and four mole equivalents of $LiBH_4$ were stirred together for 12 hours in Et_2O solution. After pumping off the solvent, and extracting the residue with benzene, the resulting green solution was filtered through celite. A green oil was left on the celite and a pale yellow solution was produced.

Yellow crystals formed in the filtrate. The ^{31}P n.m.r. spectrum of the supernatant showed that free DMPE was present, whereas comparison of the crystals with an authentic sample showed them to be the starting material, $(PhO)_2TiCl_2 \cdot DMPE$.

When the procedure was repeated with eight mole equivalents of $LiBH_4$ no starting material was recovered, but the free ligand was still observed.

Reaction of $(PhO)_2TiCl_2 \cdot DMPE$ with Sodium Amalgam

When a red solution of $(PhO)_2TiCl_2 \cdot DMPE$ in Et_2O was added to an excess of sodium amalgam the solution became colourless immediately. After shaking for 30 minutes, and filtering the supernatant, the ^{31}P n.m.r. spectrum of this solution showed one resonance corresponding to unco-ordinated DMPE. The intensity of the signal was similar to that observed for the solution of the adduct before reaction, indicating that the loss of DMPE from $(PhO)_2TiCl_2$ on reduction is almost quantitative.

Thus in all the attempted reduction reactions of phosphine adducts studied the phosphine was found not to be co-ordinated to titanium after reduction. Hence these ligands do not contribute to the stabilization of the low oxidation state species formed, which were presumably similar to those identified by Wilkinson *et al.*[181]

4.21. Experimental

Preparation of $TiCl_4 \cdot 2PEt_3$

A solution of $TiCl_4$ (50 cm^3, 0.36 mol dm^{-3}, 18.3 mmol) in benzene was added dropwise to a magnetically stirred solution of PEt_3 (50 cm^3, 0.80 mol dm^{-3}, 40 mmol) at -20°C. The solution turned dark red immediately. The temperature was allowed to room temperature and stirring was continued for a further 30 minutes. The volume of the solution was reduced by pumping to approximately one-fifth its original value and a red solid precipitated. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 2.61g, 65%).

i.r. 1460(s) 1400(w) 1380(s) 1310(w) 1260(w)
1160(w) 1045(s) 985(w) 865(s) 780(m)
768(s) 730(s) 410(w) 340(s) cm^{-1}

^{31}P n.m.r. 25.3(1) 22.3(8) 21.1(1) p.p.m.

Analysis based on $TiCl_4P_2C_{12}H_{30}$:

calculated: Ti, 11.18; C, 33.16; H, 7.06%

found: 11.95 32.01 6.63

Investigation of the $TiCl_4/PBu_3$ system by ^{31}P n.m.r. spectroscopy

$TiCl_4$ (0.1 cm^3, 0.9 mmol) was added to hexadeuterobenzene (C_6D_6) (2.5 cm^3) in a 10 mm n.m.r. tube which was placed inside a Schlenk tube PBu_3 (0.023 cm^3, 0.09 mmol) (ratio $TiCl_4:PBu_3$ = 10:1) was added to the solution and the ^{31}P n.m.r. spectrum was recorded at 36.43 MHz on a Bruker WH90 spectrometer.

Successive amounts of PBu_3 were added to the solution to decrease the ratio of $TiCl:PBu_3$ (0.023 cm^3, 5:1; 0.059 cm^3, 2:1; 0.123 cm^3, 1:1; 0.228 cm^3, 1:2; 0.683 cm^3, 1:5; 1.15 cm^3, 1:10) and a spectrum of each solution was recorded.

A similar experiment which involved the initial addition of PEt_3 to an excess of $TiCl_4$ produced an identical set of spectra.

The spectra are discussed in detail in Section 4.9.

Preparation of $TiCl_4$·DMPE

DMPE (3.34 cm^3, 20.0 mmol) was added dropwise to a magnetically stirred solution of $TiCl_4$ (2.0 cm^3, 18.3 mmol) in toluene (30 cm^3) at 0°C. An orange precipitate formed immediately. The

supernatant was removed and the solid was washed with petroleum ether (3 x 30 cm^3) and dried in *vacuo* for 4 hours (Yield 5.0g, 80%).

i.r. 1460(s) 1410(w) 1380(s) 1300(m) 1285(m)
1150(w) 1035(w) 955(s) 940(s) 920(m)
900(m) 870(w) 845(w) 790(w) 755(m)
720(s) 395(s) 365(s) 325(m) cm^{-1}

^{31}P n.m.r. 10.1 p.p.m.

Analysis based on $TiCl_4P_2C_6H_{16}$:

calculated:	Ti, 14.10;	C, 21.20;	H, 4.74%
found:	14.14	21.14	4.70

Preparation of $TiCl_4$·DBPE

DBPE (6.7 cm^3, 20.0 mmol) was added dropwise to a magnetically stirred solution of $TiCl_4$ (2.0 cm^3, 18.6 mmol) in toluene (30 cm^3) at 0°C. A red oil formed in the red solution over one hour at room temperature. The supernatant was removed and petroleum ether (50 cm^3) was added to the oil. The mixture was magnetically stirred for 72 hours when an orange powder was produced under an orange supernatant. The supernatant was removed and the solid was washed with further petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 4.95g, 85%).

i.r. 1460(s) 1380(s) 1305(s) 1225(s) 1205(m)
1090(s) 965(m) 890(m) 800(s) 720(s)
350(s) cm^{-1}

^{31}P n.m.r. 39.0 p.p.m.

Analysis based on $TiCl_4P_2C_{18}H_{40}$:

	Ti	C	H
calculated:	9.43;	42.54;	7.93 %
found:	9.25	42.67	7.98

Reaction of $TiCl_4$·DMPE with $LiBH_4$

$LiBH_4$ (0.077g, 3.53 mmol) was added to a magnetically stirred yellow solution of $TiCl_4$ (DMPE) (1.20g, 3.53 mmol) in THF (30 cm^3). The solution turned green stirring overnight. The solvent was removed by pumping and an inhomogeneous green solid resulted. This was extracted into toluene (50 cm^3) at 80°C and filtered through a pad of celite. On cooling to room temperature a brown solid precipitated from the solution. The supernatant was removed and the solid was washed with petroleum ether (3 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 0.85g).

Comparison of the infra-red spectrum of this solid with that of an authentic sample showed it to be $TiCl_3$·DMPE. Analytical data confirmed this formulation.

Analysis based on $TiCl_3P_2C_6H_{16}$:

	Ti,	C,	H,
calculated:	15.74;	23.67;	5.30%
found:	15.83	23.79	5.45

Reaction of $TiCl_4$·DMPE with sodium amalgam

A solution of $TiCl_4$·DMPE (1.50g, 4.41 mmol) in THF (50cm^3) was added to sodium amalgam (0.10g, 4.40 mol Na in 30 cm^3Hg). On shaking for 2 hours the solution turned green. The green solution was decanted from the amalgam and filtered through a pad of celite. The solvent was pumped off and an inhomogeneous green solid resulted. This was extracted into toluene (50 cm^3) at 80°C and filtered through a pad of celite. On cooling to room temperature a brown solid precipitated from the solution. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours.

Again the infra-red spectrum of this solid was identical to that of an authentic sample of $TiCl_3$·DMPE and analytical data confirmed this formulation.

Analysis based on $TiCl_3P_2C_6H_{16}$:

	Ti,	C,	H,
calculated:	15.74;	23.67;	5.30%
found:	15.87	23.76	5.46

Reaction of $TiCl_3 \cdot DBPE$ with $LiBH_4$

$LiBH_4$ (0.122g, 5.60 mmol) was added to a magnetically stirred green solution of $TiCl_3 \cdot DBPE$ (2.6g, 5.62 mmol) in THF ($30cm^3$). The solution darkened as it was stirred for 16 hours but no precipitate formed. The solution was pumped to dryness and a black oil resulted. This was extracted with benzene (50 cm^3) at 60^oC but the solution remained colourless. The ^{31}P n.m.r. spectrum of the spectrum showed one signal at -50.0 p.p.m. which was consistent with the presence of unco-ordinated DBPE.

The solid residue was inhomogeneous and insoluble in THF, Et_2O, benzene and CH_2Cl_2.

Preparation of $ZrCl_4 \cdot 2PEt_3$

PEt_3 (0.83 cm^3, 5.70 mmol) was added dropwise to a magnetically stirred suspension of $ZrCl_4$ (1.30g, 5.58 mmol) in benzene (30 cm^3). The solid dissolved immediately to give a clear, colourless solution, which was filtered through a celite pad. The volume of the solution was reduced to approximately half its original level and on standing for 16 hours white crystals formed in the solution. The supernatant was removed and the crystals were

washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 2.38g, 75%).

i.r. 1460(s) 1410(m) 1380(s) 1310(w) 1270(w)
1250(w) 1170(w) 1115(m) 1050(s) 970(w)
875(s) 780(s) 760(s) 725(s) 300(s)
cm^{-1}

^{31}P n.m.r. 21.8 p.p.m.

Analysis based on $ZrCl_4P_2C_6H_{30}$:

	Cl	C	H
calculated:	24.9;	12.66;	5.31%
found:	25.1	12.63	5.29

Preparation of $ZrCl_4 \cdot 2DMPE$

DMPE (5.17 cm^3, 31.0 mmol) was added dropwise to a magnetically stirred suspension of $ZrCl_4$ (3.55g, 15.2 mmol) in benzene (50 cm^3). The solid dissolved immediately and the resulting colourless solution was filtered through a pad of celite. On standing at room temperature for 16 hours white crystals formed. The supernatant was removed and the crystals were washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 5.27g, 65%).

i.r. 1460(s) 1415(w) 1380(s) 1295(w) 1280(w)
1130(w) 1085(s) 995(m) 940(m) 900(s)
870(m) 840(m) 740(s) 710(s) 650(m)
440(w) 340(w) 310(m) 270(s) cm^{-1}

^{31}P n.m.r. -1.2 p.p.m.

Analysis based on $ZrCl_4P_4C_{12}H_{32}$:

calculated:	Cl, 25.59;	C, 27.02;	H, 6.05%
found:	26,67	27.13	6.06

Preparation of $ZrCl_4$·DBPE

DBPE (7.12 cm^3, 19.0 mmol) was added dropwise to a magnetically stirred suspension of $ZrCl_4$ (2.10g, 9.0 mmol) in toluene (50 cm^3). The solid dissolved on heating to 80°C for 2 hours. The resulting colourless solution was filtered through a pad of celite and a white powder precipitated immediately on cooling to room temperature. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo*. (Yield 4.32g, 87%).

i.r.	1460(s)	1400(w)	1370(s)	1300(m)	1225(w)
	1130(m)	1090(m)	1015(m)	960(w)	925(m)
	840(w)	770(s)	720(s)	450(w)	300(s)

cm^{-1}

^{31}P n.m.r. 37.8 p.p.m.

Analysis based on $ZrCl_4P_2C_{18}H_{40}$

calculated:	Cl, 25.71;	C, 39.20;	H, 7.31%
found	25.43	39.95	7.50

Reaction of $ZrCl_4 \cdot 2DMPE$ and DMPE with sodium amalgam

One mole equivalent of DMPE (0.657 cm^3, 3.94 mmol) was added to a solution of $ZrCl_4 \cdot 2DMPE$ (2.10g, 3.94 mmol) in THF (50 cm^3) in an atmosphere of argon and the resulting clear solution added to an excess of sodium amalgam (0.46g, 20 mmol Na in 20 cm^3Hg). The solution quickly turned green and on shaking for 12 hours the solution turned deep red. The solution was removed from the amalgam by transfer through a stainless-steel needle under excess pressure of argon. The solution was filtered through celite, which was pretreated by heating to 120°C under reduced pressure (0.2 mm Hg) for 12 hours. The solvent was removed by pumping and the resulting red oil was extracted into pentane.

On standing at -20°C for 3 months a black precipitate formed. This was isolated by filtration. The black solid was found to be insoluble in all solvents including water and analysis indicated that the solid contained no organic matter.

After the solid was heated to a red heat a white solid was observed on cooling. The weight increase was consistent with the formation of ZrO_2 from Zirconium metal.

^{31}P n.m.r. (red solution, pentane)

-1.2 , -47.9 p.p.m.

Zr (0.034g, 0.372 mmol) → ZrO_2 (0.045g, 0.365 mmol)

Reaction of $[Zr(DMPE)_n]$ with Butadiene

Butadiene was bubbled slowly into a red solution of $[Zr(DMPE)_n]$, prepared as described above, until the solution was decolourized (5 min). The solution became very hot and a white precipitate formed. This was isolated by filtration and washed with petroleum ether (2 x 30 cm^3). The white solid was insoluble in most common solvents and analytical data was consistent with the solid being predominantly polybutadiene.

Analysis based on $[C_4H_6]_n$:

calculated:	C, 88.8;	H, 11.2%
found:	87.9	11.1

Reaction of $ZrCl_4$·DBPE with Sodium Amalgam

A suspension of $ZrCl_4$·DBPE (0.85g, 1.54 mmol) in benzene (50 cm^3) was shaken for 4 hours with one mole equivalent of sodium amalgam (0.23g, 10.0 mmol Na in 20 cm^3 Hg). The solution remained clear. It was decanted from the amalgam and filtered through celite. There was no solid residue after the benzene had been pumped off so it was likely that the product was insoluble and could not be separated from the amalgam by extraction with THF or diethyl ether.

Reaction of $ZrCl_4 \cdot 2NBu_3$ with Sodium Amalgam

NBu_3 (3.81 cm^3, 16.0 mmol) was added dropwise to a magnetically stirred suspension of $ZrCl_4$ (1.85g, 7.94 mmol) in toluene (50 cm^3). The solid dissolved immediately, but the solution darkened to a green colour.

The solution was mixed with sodium amalgam (0.182g, 7.9 mmol Na in 20 cm^3 Hg). On shaking for 4 hours the solution became intensely coloured. It was decanted from the amalgam but on standing the solution became colourless as a grey precipitate formed. The clear supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo*.

Analytical data suggested that this solid, which was insoluble in all common solvents contained a large proportion of chloride so if an adduct of the type $[ZrCl_3(NBu_3)_2]_2$ was formed it was intimately mixed with NaCl, from which it could not be separated. Analysis Cl, 45.6; C, 7.0; H, 2.1; N, 1.3%

Preparation of $ZrCl_4 \cdot TMEDA$

TMEDA (0.709 cm^3, 4.80 mmol) was added dropwise to a magnetically stirred solution of $ZrCl_4$ (1.10g, 4.72 mmol) in benzene. The solid did not dissolve

as the suspension was stirred for 7 days. The supernatant was removed and the solid was washed with petroleum ether (2 x 50 cm^3) and dried in *vacuo* for 4 hours. (Yield 1.12g, 95%).

i.r. 1460(s) 1380(s) 1300(m) 1280(m) 1230(m)
1195(w) 1170(m) 1115(m) 1095(w) 1065(w)
1040(m) 1005(s) 990(s) 980(m) 940(s)
800(s) 760(s) 720(s) 590(w) 520(m)
390(m) 340(s) 300(m) cm^{-1}

Analysis based on $ZrCl_4C_6H_{16}N_2$:

	Cl	C	H	N
calculated:	40.6;	20.63;	4.62;	8.02%
found:	40.9	21.05	4.66	7.01

Preparation of $ZrCl_4 \cdot 1.5TMEDA$

TMEDA (1.70 cm^3, 11.5 mmol) was added dropwise to a magnetically stirred solution of $ZrCl_4$ (1.34g, 5.75 mmol) in EtOAc (50 cm^3). A white precipitate formed immediately. The supernatant was removed and the solid was washed with petroleum ether (2 x 80 cm^3) and dried in *vacuo* for 4 hours. (Yield 2.10g, 90%).

i.r. 1460(s) 1380(s) 1310(s) 1250(m) 1200(w)
1190(m) 1170(w) 1150(s) 1100(w) 1080(w)
1040(w) 1020(s) 1000(s) 970(s) 860(s)
800(m) 725(s) 525(m) 435(m) 300(s)
cm^{-1}

Analysis based on $ZrCl_4C_9H_{24}N_3$:

calculated:	Cl, 34.8;	C, 26.54;	H, 5.94;	N, 12.17%
found:	35.3	27.13	6.14	12.31

Preparation of $TiCl_4$·TMEDA

TMEDA (2.87 cm^3, 19.0 mmol) was added dropwise to a magnetically stirred solution of $TiCl_4$ (2.0 cm^3, 18.3 mmol) in petroleum ether (50 cm^3). A yellow precipitate formed immediately. The supernatant was removed and the solid was washed with petroleum ether (2 x 50 cm^3) and dried in *vacuo* for 4 hours. (Yield g, 98%).

i.r.	1460(s)	1405(w)	1380(s)	1280(m)	1230(m)
	1190(w)	1110(w)	1095(w)	1065(w)	1040(m)
	1000(s)	990(m)	980(w)	945(s)	800(s)
	765(m)	725(w)	598(w)	525(w)	500(w)
	455(w)	400(m)	370(s)	300(w)	275(w)

cm^{-1}

^1H n.m.r. 2.30(s)(3H) 2.50(s)(1H) p.p.m.

Analysis based on $TiCl_4C_6H_{16}N_2$:

calculated:	Ti, 16.19;	C, 24.35;	H, 5.45;	N, 9.46%
found:	16.31	24.39	5.26	9.31

Reaction of $TiCl_4$·TMEDA with $LiBH_4$

One mole equivalent of $LiBH_4$ (0.282g, 10.3 mmol)

was added to a magnetically stirred solution of $TiCl_4 \cdot TMEDA$ (3.10g, 10.5 mmol). The solution turned green immediately. Stirring was continued for 12 hours, after which time the solution was blue. The solution was filtered through a pad of celite and left to stand at -20°C for 16 hours and blue crystals were formed. The supernatant was removed and the crystals were washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* 1 hour (Yield 0.93g, 25%).

i.r.	1460(s)	1380(s)	1290(w)	1280(m)	1240(w)
	1205(w)	1190(w)	1165(m)	1145(w)	1120(w)
	1100(w)	1065(m)	1040(m)	1010(s)	950(m)
	925(w)	860(s)	800(s)	760(w)	755(w)
	725(w)	680(w)	590(w)	510(m)	490(m)
	450(m)	390(m)	355(s)	320(s)	cm^{-1}

Analysis based on $TiCl_3C_{10}H_{24}ON_2$:

calculated:	Ti, 13.52;	C, 33.89;	H, 6.83;	N, 7.90%
found:	13.76	34.72	6.97	7.62

Blue crystals of $TiCl_3 \cdot TMEDA \cdot THF$ (1.40g, 3.95 mmol) were heated to 60°C under reduced pressure (0.1 mmHg) for 4 hours. The solid gradually became amorphous and weight loss (0.245g, 17.6%) indicated the product was $TiCl_3 \cdot TMEDA$. Analytical data was consistent with this formulation.

i.r. 1460(s) 1380(s) 1265(s) 1120(m) 1100(s)
1070(s) 1045(m) 950(m) 930(w) 800(s)
725(m) 595(w) 500(m) 480(m) 450(w)
380(m) 350(s) 320(s) cm^{-1}

Analysis based on $TiCl_3C_6H_{14}N_2$:

calculated:	Ti, 16.11;	C, 24.24;	H, 4.75;	N, 9.42%
found:	16.35	24.02	4.67	9.31

Preparation of $TiCl_3$·DMPE

DMPE (3.84 cm^3, 23.0 mmol) was added dropwise to a magnetically stirred green solution of $TiCl_3$ (3.40g, 22.0 mmol) in EtOAc (30 cm^3). The solution became brown and a brown precipitate formed when the volume of the solution was reduced to approximately half its original level. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 4.69g, 70%).

i.r. 1460(s) 1410(m) 1390(s) 1400(m) 1380(m)
1340(m) 1240(s) 1190(m) 1145(s) 950(s)
930(s) 900(m) 865(m) 840(m) 790(w)
720(s) 640(s) 610(w) 380(s) 310(m)
280(m) cm^{-1}

Analysis based on $TiCl_3C_6H_{16}P_2$

calculated:	Ti, 15.74;	C, 23.67;	H, 5.30%	
found:	15.65	23.52	5.23	

Preparation of $TiCl_3 \cdot DBPE$

DBPE (5.62 cm^3, 15.0 mmol) was added dropwise to a magnetically stirred solution of $TiCl_3$ (2.30g, 14.9 mmol) in EtOAc (30 cm^3). The solution was stirred for 16 hours and then the solvent was removed by pumping. A brown oil resulted. Petroleum ether (50 cm^3) was added to the oil and the mixture was stirred for 24 hours. A green powder was formed. The supernatant was removed and the solid was washed with further petroleum ether and dried in *vacuo* for 4 hours. (Yield 5.63g, 80%).

i.r. 1460(s) 1380(s) 1310(m) 1280(w) 1225(m)
1190(w) 1100(s) 1020(s) 970(m) 900(m)
870(w) 725(s) 640(m) 550(m) 350(s)
cm^{-1}

Analysis based on $TiCl_3C_{18}H_{40}P_2$:

calculated:	Ti, 10.13;	C, 45.73;	H, 8.53%
found:	9.96	45.97	8.62

Preparation of $(PhO)_2TiCl_2 \cdot 2PMe_3$

PMe_3 (0.585g, 7.80 mmol) was distilled into a solution of $(PhO)_2TiCl_2$ (1.25g, 3.85 mmol) in benzene at -196°C on an all-glass vacuum line. The reaction flask was closed and the temperature

was allowed to rise to that of the room and the red solution was magnetically stirred. An orange precipitate formed over a month. The reaction flask was attached to a Schlenk line and the supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 0.83g, 45%).

i.r. 1605(w) 1585(s) 1560(w) 1460(s) 1380(s)
1310(w) 1300(s) 1250(s) 1105(s) 960(m)
955(s) 890(m) 870(s) 760(s) 720(m)
690(m) 680(w) 665(m) 640(m) 625(m)
520(w) 460(w) 425(m) 395(m) 365(m)
320(m) 270(w) cm^{-1}

^{31}P n.m.r. 65.6 p.p.m.

^{1}H n.m.r. 1.75(9H)(d) 6.8-7.4(5H)(m)

Analysis based on $TiCl_2P_2C_{18}H_{28}O_2$:

calculated: Ti, 10.47; C, 47.25; H, 6.17

found: Ti, 10.51 C, 47.05; H, 6.09

Preparation of $(PhO)_2TiCl_2 \cdot 2PPh_3$

PPh_3 (1.26g, 4.80 mmol) was added to a magnetically stirred solution of $(PhO)_2TiCl_2$ (0.75g, 2.31 mmol) in Et_2O (30 cm^3). A small amount of red oil was formed under a red solution. The solution was decanted from the

oil and a golden yellow precipitate formed slowly when petroleum ether (10 cm^3) was added to the solution. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 0.69g, 35%).

i.r. 1590(s) 1460(s) 1380(s) 1240(s) 1210(m)
1160(m) 1115(m) 1070(m) 1025(w) 1000(w)
900(s) 810(w) 750(m) 725(s) 690(s)
665(m) 500(m) 460(w) 385(m) 340(s)
cm^{-1}

^{31}P n.m.r. 1.8 p.p.m.

Analysis based on $TiCl_2P_2C_{48}H_{40}O_2$:

calculated: Ti, 5.78; C, 69.5; H, 4.86

found Ti, 5.66; C, 70.3; H, 4.91

Preparation of $(PhO)_2TiCl_2 \cdot DPPE$

DPPE (2.11g, 5.30 mmol) was added to a magnetically stirred solution of $(PhO)_2TiCl_2$ (0.85g, 2.62 mmol) in Et_2O (30 cm^3). A small amount of red oil formed in an orange solution. The solution was decanted from the oil and a yellow powder precipitated when the volume of the solution was reduced by pumping. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours.

(Yield 1.23g, 65%).

i.r. 1605(w) 1590(s) 1460(s) 1380(s) 1260(m)
1230(m) 1160(m) 1120(m) 1100(w) 1070(m)
1020(m) 1000(m) 890(s) 815(w) 740(s)
725(s) 690(s) 650(m) 510(s) 450(m)
400(m) 380(s) cm^{-1}

^{31}P n.m.r. 3.7 (2) 14.5 (1)

Analysis based on $TiCl_2P_2C_{26}H_{34}O_2$:

calculated: Ti, 6.81; C, 64.87; H, 4.88 %

found: Ti, 6.71; C, 66.0; H, 4.95 %

Preparation of $(PhO)_2TiCl_2 \cdot DMPE$

DMPE (1.17 cm^3, 7.40 mmol) was added dropwise to a magnetically stirred solution of $(PhO)_2TiCl_2$ (1.20g, 3.69 mmol) in benzene (30 cm^3). The red solution turned orange over 10 minutes and a yellow precipitate formed when the volume of the solution was reduced by pumping. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 3 hours. (Yield 1.40g, 80%).

i.r. 1610(w) 1590(s) 1460(s) 1380(s) 1300(w)
1260(m) 1160(w) 1070(w) 1020(m) 1005(w)
950(m) 890(s) 800(w) 760(s) 725(s)
690(s) 660(s) 645(s) 515(m) 460(s)
420(s) 390(s) 350(s) cm^{-1}

^{31}P n.m.r. -5.5 p.p.m.

^{1}H n.m.r. 1.30 (6H)(m) 1.85 (2H)(d)

7.1 - 7.4 (5H)(m) p.p.m.

Analysis based on $TiCl_2P_2C_{18}H_{26}O_2$:

calculated: Ti, 10.53; C, 47.5; H, 5.72

found: Ti, 10.61; C, 48.3; H, 5.75

Preparation of $(PhO)_2TiCl_2 \cdot TMEDA$

TMEDA (1.15cm^3, 7.60 mmol) was added dropwise to a magnetically stirred solution of $(PhO)_2TiCl_2$ (2.45g, 7.54 mmol) in Et_2O (30 cm^3). An orange precipitate formed on standing for 16 hours. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 4 hours. (Yield 3.67g, 85%).

i.r. 1590(s) 1460(s) 1380(m) 1250(s) 1160(m)
1120(w) 1100(w) 1070(m) 1040(w) 1025(m)
1010(m) 1000(m) 950(m) 880(s) 800(s)
760(s) 690(s) 650(s) 510(m) 480(w)
455(m) 400(s) 360(s) 345(s) cm^{-1}

^{1}H n.m.r. 2.6-2.9(6H)(m) 2.9-3.1(2H)(m) p.p.m.
6.9-7.5(5H)(m)

Analysis based on $TiCl_2C_{18}H_{26}O_2N_2$:

calculated: Ti, 11.38; C, 51.33; N, 6.65; H, 6.23

found: Ti, 11.47; C, 51.25; N, 6.75; H, 6.26

Reaction of $(PhO)_2TiCl_2 \cdot DPPE$ with $LiBH_4$

$LiBH_4$ (0.088g, 4.0 mmol) was added to a magnetically stirred solution of $(PhO)_2TiCl_2 \cdot DPPE$ (0.65g, 0.90 mmol) in THF (50 cm^3). The red solution turned green as the solution was stirred for 4 hours. The solution was then pumped to dryness and the resulting inhomogeneous green oil was extracted with boiling benzene (50 cm^3) and filtered through a celite pad. On cooling white crystals formed in the green solution. The supernatant was removed and the crystals were washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo*. Comparison of the i.r. and ^{31}P n.m.r. of these crystals with those of an authentic sample showed them to be DPPE. (Yield 0.27g, 75%).

Reaction of $(PhO)_2TiCl_2 \cdot DPPE$ with Sodium Amalgam

A red solution of $(PhO)_2TiCl_2 \cdot DPPE$ (0.85g, 1.18 mmol) in Et_2O (50 cm^3) was added to sodium amalgam (0.225g, 5.0 mmol Na in 30 cm^3 Hg). The solution became colourless immediately. After shaking for 30 minutes the solution was decanted from the amalgam and filtered through a pad of celite. On standing white crystals formed in the

solution. The supernatant was removed and the solid was washed with petroleum ether (2 x 30 cm^3) and dried in *vacuo* for 2 hours.

Comparison of the i.r. and ^{31}P n.m.r. spectra of this solid with those of an authentic sample showed it to be DPPE (0.305g, 65%).

Reaction of $(PhO)_2TiCl_2 \cdot DMPE$ with $LiBH_4$

$LiBH_4$ (0.120g, 5.50 mmol) was added to a magnetically stirred solution of $(PhO)_2TiCl_2 \cdot DMPE$ (0.60g, 1.26 mmol) in Et_2O (30 cm^3). The red solution became green on stirring for 12 hours. The solution was pumped to dryness and then extracted into hot benzene (50 cm^3). On filtration through a pad of celite a colourless solution was produced and a green residue remained on the celite. The ^{31}P n.m.r. spectrum of the benzene solution showed that it contained only unco-ordinated DMPE. The concentration of the free ligand was estimated by noting the increase in intensity of the signal when a known volume of DMPE was added. (Yield 0.104g, 55%).

Reaction of $(PhO)_2TiCl_2 \cdot DMPE$ with Sodium Amalgam

A red solution of $(PhO)_2 TiCl_2 \cdot DMPE$ (1.20g, 2.53 mmol) in Et_2O)50 cm^3) was added to sodium

amalgam (0.276g, 12.0 mmol Na in 20 cm^3 Hg). The solution became colourless immediately on shaking. After shaking for 30 minutes the solution was decanted from the amalgam and filtered through a pad of celite. The ^{31}P n.m.r. spectrum of this solution showed that it contained only unco-ordinated DMPE. The concentration was estimated to be 35.4 mol dm^{-3}, by the n.m.r. method described above. (Yield 0.265g, 70%).

Appendix: The Preparation of Phosphine Ligands

Preparation of DMPE

The preparation of DMPE was first attempted by the method of Butter and Chatt[209]. This route is outlined in the equations below.

$$6MeMgI + 2PSCl_3 \rightarrow Me_2PS\text{-}PSMe_2 + 6MgClI + C_2H_6$$

$$Me_2PS\text{-}PSMe_2 + 2Fe \rightarrow Me_2P\text{-}PMe_2 + 2FeS$$

$$Me_2P\text{-}PMe_2 + 2Na \rightarrow 2Me_2PNa$$

$$2Me_2PNa + ClCH_2CH_2Cl \rightarrow Me_2PCH_2CH_2PMe_2 + 2NaCl$$

However this is not now the method of choice for many reasons. Other workers have found that the preparation of $Me_2PS\text{-}PSMe_2$ is potentially very hazardous as explosions have taken place when a Grignard reagent is mixed with $PSCl_3$[210]. The product $Me_2PS\text{-}PSMe_2$ is very toxic and many people develop a severe allergic reaction to phosphorus sulphide compounds[211].

Also the product of the desulphurization of $Me_2PS\text{-}PSMe_2$, $Me_2P\text{-}PMe_2$ is very pyrophoric and foul smelling and hence is difficult to handle.

Finally in this work only very small yields (< 1%) of DMPE were obtained from the final stage of this sequence, and the product was contaminated with pyrophoric impurities.

Preparation of Me_2PS-Me_2PS

A solution of MeMgI was prepared by adding a solution of MeI (568g, 4.0 mol) in Et_2O (750 cm^3) to a mechanically stirred suspension of magnesium metal (75.0g, 4.0 mol) in Et_2O (750 cm^3) over 6 hours at 0^oC.

$PSCl_3$ (217.0g, 1.28 mol) in Et_2O (300 cm^3) was then added dropwise over 2 hours while the solution is maintained at 0^oC with a acetone-solid CO_2 bath. After addition is complete the reaction mixture is heated to reflux for 1.5 hours. The solution was cooled to 0^oC and then decanted on to a mixture of ice (400g) and concentrated sulphuric acid (200 cm^3). The reaction flask was washed with Et_2O and the washings were also decanted onto the ice-sulphuric acid mixture. The solution was allowed to stand for 16 hours and the solid was collected on a large Buchner funnel and washed with cold water (500 cm^3) and Et_2O (250cm^3) and dried in *vacuo* for 2 hours. (Yield 82g, 82%).

Preparation of Me_2P-PMe_2

Me_2PS-$PSMe_2$ (20.1g, 0.108 mol) was intimately mixed with iron powder (40g, 0.716 mol) by grinding

the solids together with a pestle and mortar. The mixture was transferred to a distillation apparatus and gently heated with a Bunsen burner, under a nitrogen atmosphere, until a liquid was observed. Heating was continued for 10 minutes at such a level that the liquid refluxed gently. The flask is then heated more strongly so that the liquid, $Me_2P\text{-}PMe_2$ distills into a Schlenk tube (b.p. 140°C). (Yield 12.2g, 92%).

The product $Me_2P\text{-}PMe_2$ is malodorous and spontaneously flammable in air; great care had to be taken in disassembling the distillation apparatus.

A solution of I_2 in CCl_4 was cautiously added to the iron residue after it had cooled to room temperature and all glass-ware was immediately immersed in the same solution after use.

Reaction of $Me_2P\text{-}PMe_2$ with Sodium in Liquid Ammonia

A solution of sodium in liquid ammonia was prepared by adding pellets of sodium (1.21g, 50 mmol) to magnetically stirred ammonia (400 cm^3) which was maintained at -40°C with an acetone-solid CO_2 bath. The solution was then stirred for 30 minutes and then a solution of $Me_2P\text{-}PMe_2$ (6.0 g, 49 mmol) in Et_2O (50 cm^3) is added dropwise over 30 minutes

from a pressure-equalized dropping funnel. The blue solution turned green immediately and then gradually red over the period of mixing. The solution was allowed to warm to room temperature and $ClCH_2CH_2Cl$ (1.97 cm^3, 25 mmol) was added dropwise over 10 minutes. The red colour was discharged and the ammonia was allowed to evaporate over 24 hours under a stream of nitrogen.

When the solid residue was heated to distil the final mixture no liquid was apparent so the solid residue was washed with Et_2O (200 cm^3) and filtered through a pad of celite. The Et_2O was distilled at atmospheric pressure and a small amount of an oil remained. Only a small fraction of this oil boiled below 180°C when the pressure was reduced to 10 mmHg. This distillate was pyrophoric and its ^{31}P n.m.r. spectrum indicated that it was very impure DMPE. The yield was not improved when the preparation was repeated a further three times.

Preparation of $Cl_2PCH_2CH_2PCl_2$

The compound $Cl_2PCH_2CH_2PCl_2$ was prepared by the method of Chatt *et al*[211] with modifications suggested by Green[212].

This method is not totally reliable. The procedure described below was carried out six times. On two occasions none of the desired product was formed and on a further two occasions a poor yield (10 - 20g) was obtained. Hence the yields stated below refer to only two out of six experiments.

It is not known why some preparations were more successful than others as almost exactly the same procedure was followed in each attempt. However it was observed that the total pressure in the reaction vessel was never observed above 90 atm. during successful preparations but was at high as 110 atm. during preparations which failed. It was noted that the surface of the stainless steel autoclave became pitted after use which suggests that iron may act as catalyst in the reaction and hence a clean surface is required. White phosphorus (28.0g, 0.90 mol) was removed from storage under water and quickly dried with absorbent paper and placed in a wide necked Schlenk tube. It was then dried under reduced pressure (0.1 mmHg) for 3 hours.

Phosphorus trichloride (325 cm^3, 513g, 3.75 mol) was poured into a nitrogen flushed stainless steel one litre autoclave. The white phosphorus

was added quickly to the PCl_3 and the autoclave was assembled. The autoclave was then charged with 50 atm. of nitrogen and then vented in order to reduce levels of oxygen, water and HCl in the reaction vessel.

Ethylene (60 atm.) was then added to the autoclave and the system was sealed as it was shaken for 30 minutes. Over this time the pressure in the autoclave dropped to 45 atm. as ethylene dissolved in the PCl_3. The autoclave was recharged with more ethylene to 60 atm. and shaking was continued as the temperature was increased gradually to 175°C over 6 hours. It was kept at this temperature for 12 hours and then gradually increased to 220°C over a further 9 hours. The maximum pressure, 90 atm., was observed at this time but the pressure dropped to 35 atm. when the autoclave was kept at 220°C for the following 24 hours. The autoclave was then allowed to cool to room temperature over the next 16 hours.

The autoclave was opened in a fume cupboard and its contents, a brown liquid, were transferred into a one litre flask through a copper tube (1cm diameter) using an excess of nitrogen pressure. The residue in the autoclave was then washed with Et_2O (2 x 250 cm^3) and the washings were transferred

into the same flask again using excess nitrogen pressure. A brown solid residue remained in the autoclave. This was carefully treated with a concentrated aqueous solution of $CuSO_4$.

The solution containing the product was pumped on (0.1 mm Hg) for 4 hours to remove unreacted PCl_3 and Et_2O. The residue was then transferred to a distillation apparatus under nitrogen through a filter to remove some remaining brown solid from the solution.

The residue was heated at a pressure of 1mm Hg and the product, $Cl_2PCH_2CH_2PCl_2$, distilled at 100°C to give a clear viscous liquid. (Yield 115g) (^{31}P n.m.r. 33.4 p.p.m.).

Preparation of DMPE using a Grignard Reagent

A solution of CH_3Br (129g, 1.36 mol) in Et_2O(250 cm^3), was added dropwise over 2 hours to a mechanically stirred suspension of magnesium metal (35.0g, 1.44 mol) in Et_2O (1.5 dm^3) in a three litre flask, which was cooled to -20°C in an acetone/solid CO_2 bath. Almost all the magnesium dissolved during this period and the solution was stirred at room temperature for 30 minutes to ensure completion of the preparation of CH_3MgBr.

The solution was then cooled to -30°C and a solution of $Cl_2PCH_2CH_2PCl_2$ (61.0g, 0.263 mol) in Et_2O (150 cm^3) was added dropwise over 45 minutes, during which time a white precipitate formed. The temperature was allowed to rise to room temperature and an aqueous solution of NH_4Cl (75g, 300 cm^3) was added slowly to hydrolyse excess CH_3MgBr and the precipitate dissolved.

The Et_2O solution was separated from the aqueous layer by transfer to a three litre flask through a stainless steel needle using an excess pressure of nitrogen. The aqueous layer was washed with Et_2O (300 cm^3) and the combined Et_2O solutions were dried over $MgSO_4$ (30g) for 16 hours.

The solution was then filtered and the Et_2O was distilled at atmospheric pressure (35°C). When the bulk of the Et_2O had been removed the solution was transferred to a smaller distillation apparatus and the remainder of the Et_2O was distilled from the solution.

The pressure was then reduced (10 mm Hg) and DMPE distilled at 66°C into a Schlenk tube cooled in solid CO_2. (Yield 33.5g, 85%) (^{31}P n.m.r. -47.9 p.p.m.)

Preparation of DMPE using Methyl Lithium

A solution of MeLi in Et_2O (193 cm^3, 1.4 mol dm^3, 0.27 mol) was added dropwise over 1.5 hours to a mechanically stirred solution of $Cl_2PCH_2CH_2PCl_2$ (14g, 0.060 mol) in Et_2O (300 cm^3) which was cooled to -20°C in an acetone/solid CO_2 bath. A white precipitate was formed immediately which became denser as addition continued.

The temperature was allowed to rise to room temperature and the solution was stirred for 30 minutes. The solution was cooled to -30°C and degassed water (300 cm^3) was added dropwise over 30 minutes. The white precipitate dissolved but little bubbling was observed.

After warming to room temperature the ether layer was transferred to a two litre flask using an excess of nitrogen pressure. The aqueous layer was washed with Et_2O (250 cm^3) and the combined ether layers were dried and distilled as described above. (Yield 4.95g, 55%).

Preparation of DBPE

DBPE was prepared by similar routes to DMPE.

(i) A solution of BuMgI in Et_2O was prepared by adding BuI (89.3g, 0.48 mol) in Et_2O (50 cm^3)

dropwise over 1 hour to a mechanically stirred suspension of magnesium metal (120g, 0.49 mol) in Et_2O (500 cm^3) at -20°C. A solution of $Cl_2PCH_2CH_2PCl_2$ (25.0g, 0.108 mol) in Et_2O (250 cm^3) was added dropwise over 30 minutes and a fine white precipitate formed. The solution was allowed to warm to room temperature. After stirring for 30 minutes the solution was cooled to - 20°C in an acetone/solid CO_2 bath and a degassed saturated aqueous solution of NH_4Cl (50g, 200 cm^3) was added in order to hydrolyse excess BuMgI.

The precipitate dissolved and after warming to room temperature the Et_2O layer was transferred to a one litre flask through a stainless steel needle using an excess pressure of nitrogen. The aqueous layer was washed with Et_2O (200 cm^3) and the combined Et_2O fractions were dried over $MgSO_4$ (25 g) and then filtered. The Et_2O was removed by pumping (0.1 mm Hg) on the solution for 4 hours. A viscous oil remained which was transferred to distillation apparatus. The product, DBPE distilled at 130°C, 0.25 mm Hg, though a dark residue remained in the flask. (Yield 15.8g, 45%) (^{31}P n.m.r. -27.9 p.p.m.)

(ii) DBPE was prepared from $Cl_2PCH_2CH_2PCl_2$ and butyl lithium by following the procedure described above for the preparation of DMPE using methyl lithium.

The product was isolated and distilled as described immediately above. (Yield 8.80g, 25%).

Therefore DMPE and DBPE were both successfully prepared from $Cl_2PCH_2CH_2PCl_2$ and either an appropriate Grignard reagent of lithium alkyl.

$$Cl_2PCH_2CH_2PCl_2 + 4RMgX \rightarrow R_2PCH_2CH_2PR_2 + 4MgXCl$$
(R = Me, Bu)

$$Cl_2PCH_2CH_2PCl_2 + 4RLi \rightarrow R_2PCH_2CH_2PR_2 + 4LiCl$$
(R = Me, Bu)

However the yields were consistently better using Grignard reagent rather than the solutions of lithium alkyls. This may have been because the Grignard solutions were always freshly prepared, whereas the lithium alkyl solutions were obtained commercially and may have contained traces of lithium hydroxide which would complicate the reaction.

$$LiOH + Cl_2PCH_2CH_2PCl_2 \rightarrow (HO)ClPCH_2CH_2PCl_2 + LiCl$$

The ^{31}P n.m.r. spectrum of a solution of $Cl_2PCH_2CHPCl_2$ and four and a half mole equivalent of butyl lithium shows several resonances, in two major groups. One set between -27 and -35 p.p.m. are due to alkyl phosphines, including DBPE but another set of resonances between 25 and 60 p.p.m. are probably due to phosphorus bonded to chloride or hydroxide. Thus the desired compound is only a small proportion of the total mixture.

Preparation of PEt_3

A solution EtMgBr was prepared by adding a solution of EtBr (240g, 2.20 mol) dropwise over 2 hours to a mechanically stirred suspension of magnesium metal (18.0g, 0.74 mol) in Et_2O (2 dm^3), maintained at -30°C by an acetone/solid CO_2 bath. The temperature was allowed to rise to room temperature and the solution was stirred for 1 hour.

The solution was then cooled to -30°C and a solution of PBr_3 (63 cm^3, 0.664 mol) in Et_2O (100 cm^3) was added dropwise over 3 hours and a white precipitate formed. After addition was complete the solution was heated to reflux temperature for 1 hour.

The solution was then cooled to -20°C and a degassed aqueous solution of NH_4Cl (20g, 800 cm^3 H_2O) was added dropwise over 30 minutes in order to hydrolyse excess EtMgBr. The Et_2O layer was transferred to a three litre flask through a stainless steel needle using an excess of nitrogen pressure. The aqueous layer was washed with further Et_2O (500 cm^3) and the combined Et_2O fractions were dried over $MgSO_4$ (40g) for 16 hours.

The Et_2O solution was filtered into a distillation apparatus and the Et_2O was distilled at atmospheric pressure. The remaining liquid was transferred to a smaller distillation apparatus and the product, PEt_3 was the only fraction and distilled at 120°C at atmospheric pressure. (Yield 25.5g, 32%).

Preparation of PMe_3

Trimethyl phosphine was prepared by the previously reported method[213].

PCl_3 (23.0g, 0.167 mol) in Et_2O (150 cm^3) was cooled to -78°C in a solid CO_2/acetone bath and MeLi in Et_2O (333 cm^3, 1.50 mol dm^{-3}, 0.50 mol) was added dropwise over one hour, with mechanical stirring. The temperature was

allowed to rise to 0°C and water (150 cm^3) was added over 10 minutes. The ether and aqueous layers were separated, and the ether layer was added to a saturated aqueous solution of KI/AgI (250g KI, 38.7g AgI, 150cm^3 H_2O). A white precipitate of $[AgI \cdot PMe_3]_4$ formed on shaking. This was collected and washed with saturated KI solution (150 cm^3), water (250 cm^3) and Et_2O (200 cm^3) and dried in *vacuo* for 4 hours. (Yield 17.5g, 34%).

The free phosphine, PMe_3, was prepared quantitatively by heating the complex $[AgI \cdot PMe_3]_4$ to 200°C in *vacuo*.

Starting Materials, Analytical Techniques and Instrumentation

Most of the compounds studied in this thesis are moisture or oxygen sensitive, and thus had to be handled in a dry, inert atmosphere of nitrogen, or where stated argon gas. This was achieved by using standard Schlenk techniques and a nitrogen filled dry box. When necessary reagents and solvents were pre-purified and dried by the methods outlined below.

Starting Materials

Amines

TMEDA and NBu_3 were supplied by B.D.H. Ltd., and distilled from KOH prior to use.

Aromatic Solvents

Benzene and toluene were supplied by Fisons Ltd. Both were stored over Na wire, and distilled from CaH_2 prior to use.

Carboxylic Acids

Acetic, trimethyl acetic, and benzoic acids (AR Grade) were supplied by B.D.H. Ltd. Acetic acid was distilled from P_2O_5, and CrO_3 prior to use.

Chlorinated Solvents

CH_2Cl_2, $CHCl_3$ and CCl_4 were supplied by May

and Baker Ltd., and distilled from CaH_2 prior to use.

Diethyl Ether

Et_2O was supplied by May and Baker Ltd. It was stored over Na wire, and distilled prior to use.

Esters

The esters EtOAc, EtOFm, DES, and DEM were supplied by B.D.H. Ltd. Prior to use they were dried with P_2O_5, and distilled onto 4A Lindeman molecular sieves.

DIBP was supplied by I.C.I. PLC and stored over 3A Lindeman molecular sieves, and spurged with nitrogen prior to use.

Lithium Alkyls

MeLi and BuLi were supplied by Aldrich Chemical Co., as solutions in Et_2O, and were used without further purification.

Lithium Borohydride

$LiBH_4$ was supplied by Aldrich Chemical Co. Inc., and extracted into Et_2O using a Soxhlet apparatus prior to use.

Metal Chlorides

Anhydrous $MgCl_2$ was supplied by I.C.I. PLC and not purified further, prior to use. Some samples used initially were supplied by B.D.H. Ltd.

$TiCl_4$, $SnCl_4$, $ThCl_4$, and VCl_3 were supplied by

B.D.H. Ltd., and were not further purified.

$TiCl_3$ was supplied by I.C.I. PLC and was extracted into EtOAc using a Soxhlet apparatus prior to use.

Commercial samples of $ZrCl_4$ and $HfCl_4$ were not found to be suitable for these studies, due to their unreactivity. These solids were prepared by the methods outlined below.

Preparation of $ZrCl_4$

Zirconium metal (10.3g, 0.113 mol) supplied by Ventron G.M.B.H., was heated in a silica tube to 450°C over 2 hours, under a stream of nitrogen. At this temperature pre-dried chlorine gas replaced the nitrogen stream. The white solid, $ZrCl_4$ slowly sublimed out of the tube into a flask. It was essential that the sublimation was aided by heating the silica tube with a Bunsen burner, or the tube became blocked with a plug of solid.

The temperature rose to 600°C during the reaction. Solid continued to sublime from the tube for 6 hours. After this time the flask was quickly removed from the silica tube and attached to a Schlenk line. It was pumped on for 12 hours to remove traces of Cl_2 gas.

B.D.H. Ltd., and were not further purified.

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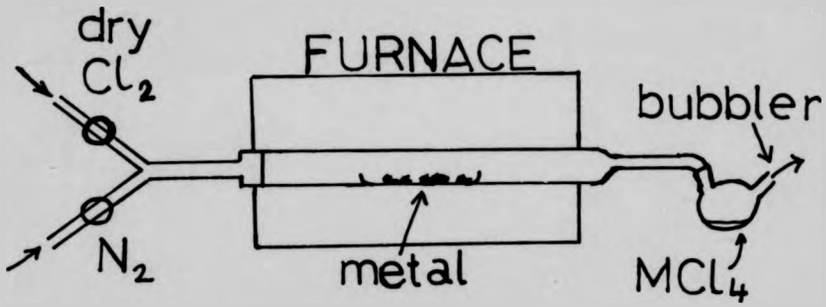
The temperature rose to 600°C during the reaction. Solid continued to sublime from the tube for 6 hours. After this time the flask was quickly removed from the silica tube and attached to a Schlenk line. It was pumped on for 12 hours to remove traces of Cl_2 gas.

After cooling 4.0g of unreacted zirconium metal was recovered from the tube. (10.3g Zr used, 4.0g recovered, yield $ZrCl_4$: 14.0g, 87%)

Analysis based on $ZrCl_4$

expected:	60.9	: Cl
found:	61.3	



The gases were dried by being passed through concentrated sulphuric acid, silica and P_2O_5.

Preparation of $HfCl_4$

Hafnium tetrachloride was prepared directly from the elements using the method described above for the preparation of $ZrCl_4$, except that the solid product did not sublime until the system was heated to 800°C.

(8.50g Hf used, 2.3g Hf recovered, yield 10.2g, 92%)

Analysis based on $HfCl_4$

expected	42.3	% Cl
found	42.0	

Preparation of Bis-phenoxy titanium(IV)dichloride

$(PhO)_2TiCl_2$ was prepared by refluxing PhOH (15.4g, 0.164 mol) with $TiCl_4$ (9.0cm^3, 82 mmol) in CCl_4 (75 cm^3) for 4 hours. A red solid formed, which was recovered by distilling off the solvent, washing with petroleum ether (2 x 200 cm^3) and drying in *vacuo* for 4 hours. (Yield 13.1g, 78%)

Methanol

MeOH was supplied by B.D.H. Ltd., and distilled from magnesium metal, then CaH_2, and stored over 4A Lindeman molecular sieves prior to use.

Petroleum Ether

Unless otherwise stated the petroleum ether used in the course of this work boiled in the range 60 - 80°C. This was supplied by May and Baker Ltd. It was distilled from Na wire prior to use.

Petroleum ether (b.p. 180°C) (E.C. 180) was supplied by Erdolchemie and was distilled from Na wire under reduced pressure prior to use.

Phosphines

The preparations of the phosphines PMe_3, PEt_3, DMPE and DBPE are described in the Appendix to Chapter 4.

PBu_3 was supplied by Strem Chemicals Inc., and was not purified further.

PPh_3 and DPPE were supplied by B.D.H. Ltd., and both were used as supplied.

Sodium amalgam

Sodium amalgam was prepared by immersing a weighed amount of sodium metal, on the end of a spatula, in mercury under an argon atmosphere until the sodium dissolved.

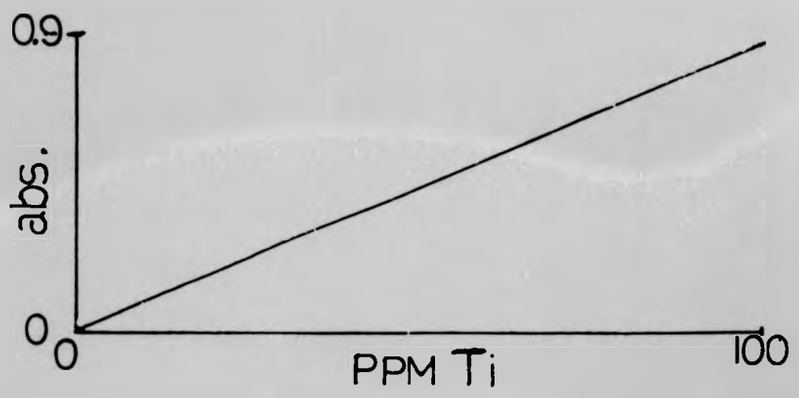
Tetrahydrofuran

THF was supplied by Fisons Ltd., and was distilled from the blue sodium benzophenone ketal prior to use.

Analytical Techniques

Titanium was determined by utilizing the adsorbance of titanium(IV) peroxo-species at 410 n.m. in acid solution. Between concentrations of 10 - 100 p.p.m. Ti these yellow solutions obey the Beer-Lambert laws.

A small amount of the test sample (0.01-0.1g) was hydrolysed with conc. H_2SO_4. The volume of the solution was made up to 100 cm^3 with distilled water and a drop of 20 vol. H_2O_2. The absorbance of the resulting yellow solution was measured with a Pye-Unicam SP-600 Spectrophotometer in a 1 cm cuvette, and compared with standards, using the graph shown below.



Magnesium and tin were both determined by atomic absorption spectrophotometry, using a Varian AA6 instrument. The optimum conditions for the determination of each element are presented in the Table below.

	element	
conditions	Mg	Sn
conc. range (p.p.m.)	0.5 - 2.0	50 - 200
wavelength (nm)	285.4	235.6
lamp current (mA)	3.0	8.0
fuel: C_2H_2/N_2O	3.0 / 3.4	4.1/3.4
burner height	9	10

The test solutions were prepared by dissolving an appropriate amount of sample in conc. H_2SO_4, adding 5 cm^3 of a standard solution of $KHSO_4$ (80g $KHSO_4$, 40 cm^3 H_2SO_4, 400 cm^3 H_2O) and making the total volume up to 100 cm^3 with distilled water. The instrument was continually calibrated against solutions made up from commercially available standard solutions (Spectrosol, B.D.H.Ltd.)

Chloride was determined by the Volhard method. The test sample (~ 0.1g) was hydrolysed with dilute HNO_3 and made up to 100 cm^3. Excess $AgNO_3$ solution was added to aliquots of the test solution and the resulting precipitate of AgCl coagulated with nitro-

benzene. The unreacted $AgNO_3$ was then titrated against standard KSCN solution, with a drop of $[NH_4][Fe(SO_4)_2]$ as indicator. The solution goes red at the end points as $[Fe(SCN)_6]^{3-}$ is formed.

Carbon, hydrogen and nitrogen were determined commercially by Elemental Micro-Analysis Ltd., Beaworthy, Devon.

Instrumentation

Routine ^{13}C and ^{31}P n.m.r. spectra (22.63 and 36.43 MHz respectively) were recorded with broad band proton decoupling, using a Bruker WH90 spectrometer.

High resolution and variable temperature ^{1}H and ^{31}P n.m.r. spectra (400 and 162 MHz, respectively) were recorded using a Bruker WH400 spectrometer, as were ^{17}O n.m.r. spectra (54.2 MHz).

All samples for n.m.r. spectroscopy were solutions in $CDCl_3$, unless otherwise stated.

Infra-red spectra were recorded in the range 4000-200 cm^{-1} using a Perkin-Elmer 580B spectrophotometer, as mulls in nujol between CsI plates, unless otherwise stated.

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